Cationic Alkylaluminum-Complexed Zirconocene Hydrides – NMR-Spectroscopic Identification, Crystallographic Structure Determination and Interconversion with Other Zirconocene Cations.

Steven M. Baldwin,[†] John E. Bercaw,[*, †] Lawrence M. Henling, [†] Michael W. Day, [†]
and Hans H. Brintzinger*[,‡]

Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, USA,
and Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany
E-mail: Bercaw@caltech.edu; Hans.Brintzinger@uni-konstanz.de

Supporting Information

[†] California Institute of Technology
[‡] Universität Konstanz

1. General Considerations

All operations were carried out under a protective dinitrogen atmosphere, either in a glovebox or on a vacuum manifold. Benzene-d_6, toluene-d_8 and other solvents used were dried by vacuum transfer either from sodium/benzophenone or from "titanocene".[1] Zirconocene complexes used as starting materials were either purchased from Strem Chemicals, Newburyport or prepared in our laboratories according to published procedures (see Table 1 of the text). Trimethylaluminum, triisobutylaluminum, diisobutylaluminum hydride, diisobutylaluminum chloride and trioctylaluminum were used as obtained from Aldrich Chemical Company, Milwaukee. Lithium aluminum hydride was obtained from Aldrich Chemical Company and purified prior to use (see below). MAO was obtained as a 30% toluene solution from Albermarle and dried at 50 ºC for 3 hours under vacuum to yield a free flowing white powder.

NMR spectra were obtained using Varian Inova 500 or Mercury 300 spectrometers. Chemical shifts are referenced to residual solvents peaks, 7.16 ppm for benzene and 7.00 ppm for the central aromatic proton resonance of toluene. UV-vis spectra were recorded on an Agilent 8453 spectrometer. X-ray diffraction data were collected on a Bruker KAPPA APEXII X-ray diffractometer.

2. Synthesis of $HAlMe_2$

$HAlMe_2$ was synthesized in analogy to previous literature[2]. Commercial $LiAlH_4$ was purified by extraction of the gray commercial solid with Et_2O in a swivel frit on the high-vacuum line. The clear solution was filtered and then the Et_2O was removed *in vacuo* to yield pure $LiAlH_4$ as a white powder. In a glove box a 50 mL pear-shaped flask was charged with 1.2 g (32 mmol) of purified $LiAlH_4$ and 2.7 mL (28 mmol, 0.9 equiv) of $AlMe_3$. A swivel frit was attached and the

apparatus was taken to the high-vacuum line, where 15 mL benzene was vacuum-transferred in from a storage flask containing sodium/benzophenone. The mixture was heated to 75 ºC under argon with stirring for 2 hours, filtered hot and then cooled in an ice bath. Benzene was removed *in vacuo* to yield $HAlMe_2$ as a viscous oil which was stored in the glove box. (***CAUTION***: all alkyl aluminum reagents used in this synthesis are pyrophoric and the $LiAlH_4$ residue, if it still contains any Et_2O, is also extremely pyrophoric)

3. Reactions of metallocene dichloride complexes with HAl^iBu_2 and $[Ph_3C][B(C_6F_5)_4]$.

Each zirconocene dichloride was weighed in a glove box into a 1-dram vial and 0.7 mL of benzene-d_6 was added. Then 5 or 10 equiv of neat HAl^iBu_2 were syringed in via microliter syringe. The vial was capped and shaken to dissolve the zirconocene dichloride and form the respective neutral hydride species. 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ was weighed into a second vial. The neutral zirconocene solution was added and the solution was mixed to generate the cationic hydride species. The solution was then transferred to a J-Young NMR tube for NMR analysis. ^{19}F NMR spectra were identical for all species studied, showing three characteristic signals for the uncomplexed $[B(C_6F_5)_4]^-$ anion at -126.68 (br, 8F), -157.32 (t, 4F 21 Hz) and -161.19 ppm (br, 8F). Therefore, only ^1H NMR spectra are reported. In each case only a single product was observed by NMR.

[*rac*-(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 2.0 mg (0.0045 mmol) *rac*-Me_2Si(1-indenyl)$_2$ $ZrCl_2$, 4.0 μL (0.022 mmol, 5 equiv) HAl^iBu_2 and 4.1 mg (0.0044 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^1H NMR (500 MHz, benzene-d_6) δ 7.34 (d, $^3J_{HH}$ = 9 Hz, 4H, Ar-H), 6.71 (m, 2H, Ar-H), 6.63 (m, 2H, Ar-H), 6.41 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 5.57 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 1.77 (n, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Bu-CH), 0.94 (t, $^3J_{HH}$ = 7 Hz, 24H, ^{i}Bu-CH_3), 0.65 (s, 4H, $Si(CH_3)_2$), 0.34 (m, 1H, Zr-

H_2), 0.26 (dd, $^3J_{HH}$ = 14, 7 Hz, 4H, ^{i}Bu-CH_2), 0.15 (dd, $^3J_{HH}$ = 14, 7 Hz, 4H, ^{i}Bu-CH_2), -2.25 (d, $^2J_{HH}$ = 8 Hz, 2H, Zr-H_2).

[*rac*-(EBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.3 mg (0.0031 mmol) *rac*-C_2H_4(1-indenyl)$_2ZrCl_2$, 3.0 μL (0.016 mmol, 5 equiv) HAl^{i}Bu$_2$ and 3.0 mg (0.0033 mmol, 1 equiv) of [Ph_3C][B(C_6F_5)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.45 (m, 2H, Ar-H), 6.81 (m, 4H, Ar-H), 6.55 (s, 2H, Ar-H), 5.73 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 5.55 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 3.32 (m, 4H, C_2H_4), 3.04 (m, 3H, C_2H_4), 1.75 (m, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH), 0.93 (m, ^{i}Bu-CH_3), 0.19 (dd, $^3J_{HH}$ = 7, 3 Hz, 13H, ^{i}Bu-CH_2), -0.29 (t, $^2J_{HH}$ = 8 Hz, 1H, Zr-H), -1.73 (d, $^2J_{HH}$ = 8 Hz, 2H, Zr-H_2).

[*rac*-(EBTHI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.4 mg (0.0033 mmol) *rac*-C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$_2ZrCl_2$, 3.0 μL (0.016 mmol, 5 equiv) HAl^{i}Bu$_2$ and 3.1 mg (0.0034 mmol, 1 equiv) of [Ph_3C][B(C_6F_5)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.80 (d, $^3J_{HH}$ = 3 Hz, 2H, Ar-H), 5.26 (d, $^3J_{HH}$ = 3 Hz, 2H, Ar-H), 3.97 (m, 1H), 3.33 (m, 1H), 2.70 (m, 2H), 2.47 (m, 4H), 2.18 (m, 6H), 1.88 (n, 7 Hz, ^{i}Bu-CH), 1.55 (m, 2H), 1.30 (m, 7H), 0.97 (dt, $^3J_{HH}$ = 9, 5 Hz, ^{i}Bu-CH_3), 0.35 (m, ^{i}Bu-CH_2), -0.47 (d, $^2J_{HH}$ = 6 Hz, 2H, Zr-H_2), -1.09 (t, $^2J_{HH}$ = 6 Hz, 1H, Zr-H).

[*rac*-Me$_2$C(1-indenyl)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.7 mg (0.0039 mmol) *rac*-Me_2C(1-indenyl)$_2ZrCl_2$, 3.5 μL (0.020 mmol, 5 equiv) HAl^{i}Bu$_2$ and 3.5 mg (0.0038 mmol, 1 equiv) of [Ph_3C][B(C_6F_5)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.29 (d, $^3J_{HH}$ = 9 Hz, 2H, Ar-H), 6.62 (m, 4H, Ar-H), 6.35 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 5.33 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 1.76 (m, 4H, ^{i}Bu-CH), 1.69 (s, 3H, $C(CH_3)_2$), 0.91 (dd, $^3J_{HH}$ = 6, 4 Hz, 24H, ^{i}Bu-CH_3), 0.80 (m, Zr-H), 0.25 (qd, $^3J_{HH}$ = 15, 7, 7 Hz, 8H, ^{i}Bu-CH_2), -1.72 (d, $^2J_{HH}$ = 7 Hz, 2H, Zr-H_2).

[Me$_4$C$_2$(C$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.2 mg (0.0032 mmol) $Me_4C_2(C_5H_4)_2ZrCl_2$, 3.0 μL (0.016 mmol, 5 equiv) HAl^{i}Bu$_2$ and 3.0 mg (0.0033 mmol, 1 equiv) of [Ph_3C][B(C_6F_5)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.95 (pt, $^3J_{HH}$ = 2 Hz, 4H, C_5-H), 5.73 (t, $^3J_{HH}$ = 2 Hz, 4H, C_5-H), 1.86 (m, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Bu-CH), 0.94 (t, $^3J_{HH}$ = 9 Hz, 24H, ^{i}Bu-CH_3), 0.88 (s, 16H, $C_2(CH_3)_4$),

0.36 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Bu-CH_2), -1.37 (d, $^2J_{HH}$ = 7.3 Hz, 2H, Zr-H_2), -1.60 (t, $^2J_{HH}$ = 7.5 Hz, 1H, Zr-H).

[$Me_2Si(C_5H_4)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$. 12.6 mg (0.0362 mmol) $Me_2Si(C_5H_4)_2ZrCl_2$, 32.2 μL (0.181 mmol, 5 equiv) HAl^iBu_2 and 33.4 mg (0.0362 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 6.22 (s, 4H, C_5-H), 5.24 (s, 4H, C_5-H), 1.83 (m, ^{i}Bu-CH), 0.94 (m, ^{i}Bu-CH_3), 0.35 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH_2), 0.17 (s, 6H, $Si(CH_3)_2$), -1.22 (t, $^2J_{HH}$ = 8 Hz, 1H, Zr-H), -2.02 (d, $^2J_{HH}$ = 8 Hz, 2H, Zr-H_2).

[$(Me_2Si)_2(C_5H_3)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$. 1.0 mg (0.0025 mmol) $(Me_2Si)_2(C_5H_3)_2$ $ZrCl_2$, 4.4 μL (0.025 mmol, 10 equiv) HAl^iBu_2 and 2.3 mg (0.0025 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 6.49 (d, $^3J_{HH}$ = 3 Hz, 4H, C_5-H), 5.94 (t, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 1.82 (m, ^{i}Bu-CH), 0.92 (m, ^{i}Bu-CH_3), 0.34 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH_2), -0.08 (s, 6H, $Si(CH_3)_2$), -1.04 (t, $^2J_{HH}$ = 7 Hz, 1H, Zr-H), -2.03 (d, $^2J_{HH}$ = 7 Hz, 2H, Zr-H_2).

[$(C_5H_5)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$. 2.3 mg (0.0079 mmol) $(C_5H_5)_2ZrCl_2$, 7.0 μL (0.039 mmol, 5 equiv) HAl^iBu_2 and 7.3 mg (0.0079 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.59 (s, 10H, C_5-H), 1.81 (n, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Bu-CH), 0.92 (d, $^3J_{HH}$ = 7 Hz, 24H, ^{i}Bu-CH_3), 0.28 (d, $^3J_{HH}$ = 7 Hz, 8H, ^{i}Bu-CH_2), -2.27 (d, $^2J_{HH}$ = 8 Hz, 2H, Zr-H_2), -2.39 (t, $^2J_{HH}$ = 8 Hz, 1H, Zr-H_2).

[$(^nBuC_5H_4)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$. 2.9 mg (0.0072 mmol) $(^nBuC_5H_4)_2ZrCl_2$, 6.4 μL (0.036 mmol, 5 equiv) HAl^iBu_2 and 6.5 mg (0.0070 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.73 (m, 4H, C_5-H), 5.67 (m, 4H, C_5-H), 2.16 (t, $^3J_{HH}$ = 7 Hz, 5H, C_5-^{n}Bu), 1.86 (m, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH), 1.20 (m, 16H, C_5-^{n}Bu), 0.96 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH_3), 0.88 (t, $^3J_{HH}$ = 7 Hz, 15H, C_5-^{n}Bu), 0.40 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH_2), -1.61 (d, $^2J_{HH}$ = 8 Hz, 2H, Zr-H_2), -1.96 (t, $^2J_{HH}$ = 8 Hz, 1H, Zr-H).

[(Me$_3$SiC$_5$H$_4$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.6 mg (0.0037 mmol) (TMSC$_5$H$_4$)$_2$ZrCl$_2$, 3.3 μL (0.019 mmol, 5 equiv) HAl^{i}Bu$_2$ and 3.5 mg (0.0038 mmol, 1 equiv) of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 6.11 (s, 4H, C$_5$-H), 6.01 (s, 4H, C$_5$-H), 1.87 (m, 4H, ^{i}Bu-CH), 0.95 (d, J = 6 Hz, ^{i}Bu-CH$_3$), 0.46 (m, ^{i}Bu-CH$_2$), 0.03 (s, 18H, C$_5$-SiMe$_3$), -1.84 (d, $^2J_{HH}$ = 9 Hz, 2H, Zr-H$_2$), -2.30 (br, 1H, Zr-H).

[(1,2-Me$_2$C$_5$H$_3$)$_2$Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.0 mg (0.0029 mmol) (1,2-Me$_2$C$_5$H$_4$)$_2$ ZrCl$_2$, 5.1 μL (0.029 mmol, 10 equiv) HAl^{i}Bu$_2$ and 2.6 mg (0.0028 mmol, 1 equiv) of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.86 (m, 2H, C$_5$-H), 5.29 (d, $^3J_{HH}$ = 3 Hz, 4H, C$_5$-H), 1.88 (m, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH), 1.74 (s, 12H, C$_5$-CH$_3$), 0.97 (d, $^3J_{HH}$ = 6 Hz, ^{i}Bu-CH$_3$), 0.43 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH$_2$), -1.42 (d, $^2J_{HH}$ = 7 Hz, 2H, Zr-H$_2$), -1.79 (br, 1H, Zr-H).

[(C$_5$H$_5$)$_2$Hf(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 4.3 mg (0.0113 mmol) (C$_5$H$_5$)$_2$HfCl$_2$, 20.2 μL (0.113 mmol, 10 equiv) HAl^{i}Bu$_2$ and 10.4 mg (0.0113 mmol, 1 equiv) of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.48 (s, 10H, C$_5$-H), 1.80 (m, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Bu-CH), 0.92 (d, $^3J_{HH}$ = 7 Hz, ^{i}Bu-CH$_3$), 0.26 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Bu-CH$_2$), -1.40 (d, $^2J_{HH}$ = 6 Hz, 2H, Zr-H$_2$), -2.27 (t, $^2J_{HH}$ = 6 Hz, 1H, Zr-H).

Attempted synthesis of [(C$_5$H$_5$)$_2$Ti(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 4.5 mg (0.0181 mmol) (C$_5$H$_5$)$_2$TiCl$_2$ and 32 μL (0.18 mmol, 10 equiv) were combined in benzene-d_6 in a J Young tube; this resulted in bubbling and a lavendar solution. ^{1}H NMR (300 MHz, benzene-d_6) δ 4.49 (s, H$_2$).

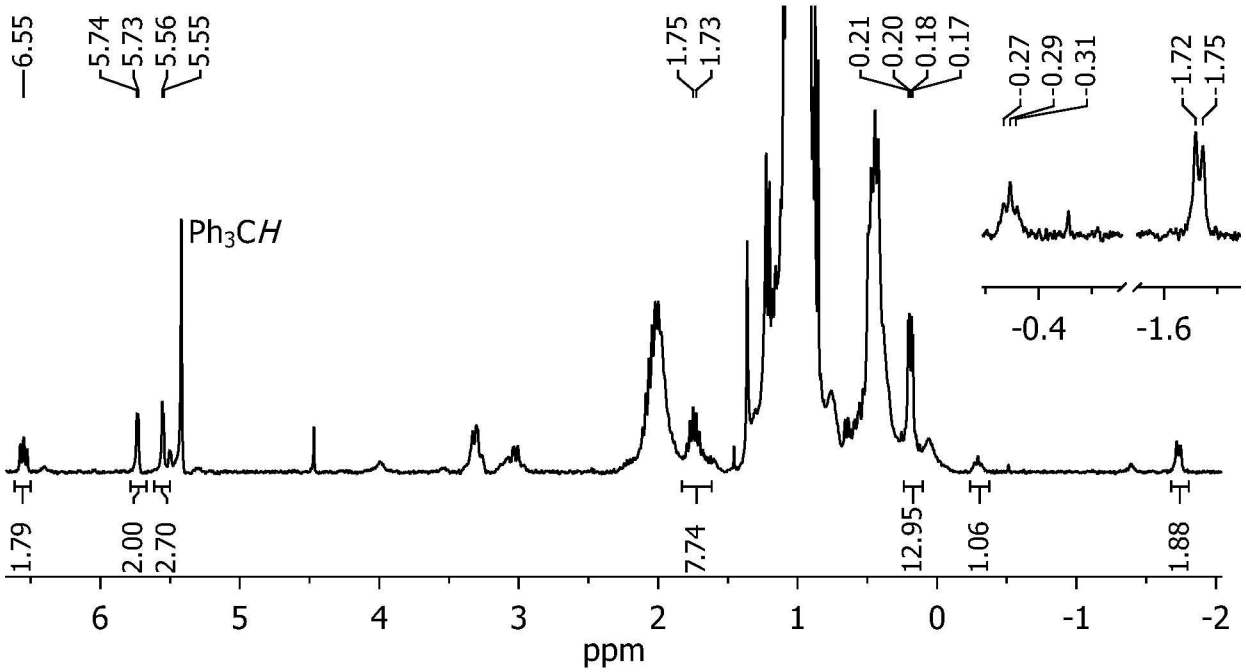

Figure S-1: ^{1}H NMR of 4.4 mM solution of [(EBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$] in benzene-d_6 prepared with 5 equiv of HAl^{i}Bu$_2$.

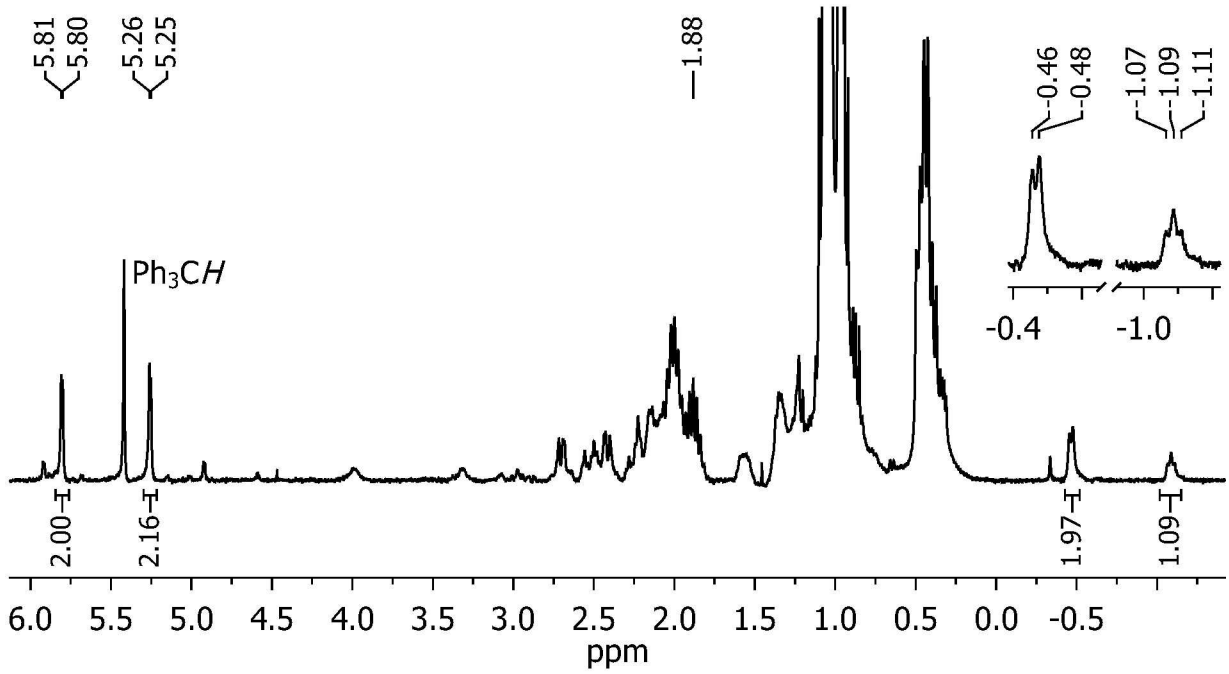

Figure S-2: ^{1}H NMR of 4.7 mM solution of [(EBTHI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$] in benzene-d_6 prepared with 5 equiv of HAl^{i}Bu$_2$.

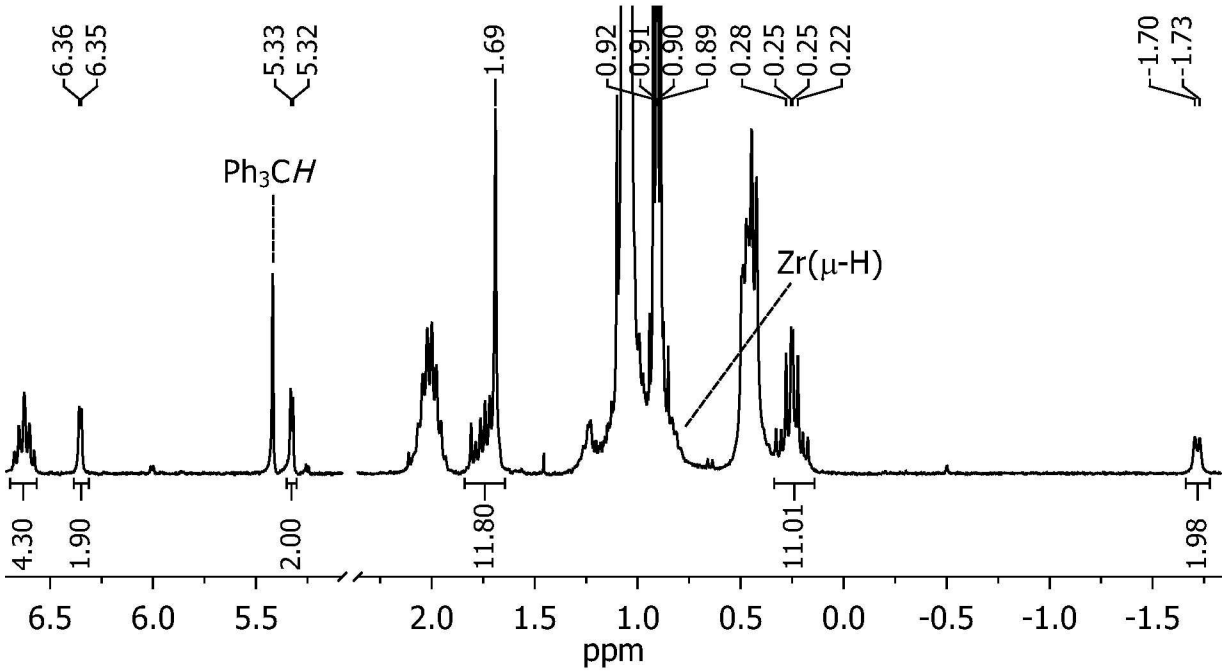

Figure S-3: ^{1}H NMR of 5.6 mM solution of $[Me_2C(1\text{-indenyl})_2Zr(\mu\text{-}H)_3(Al^{i}Bu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of $HAl^{i}Bu_2$.

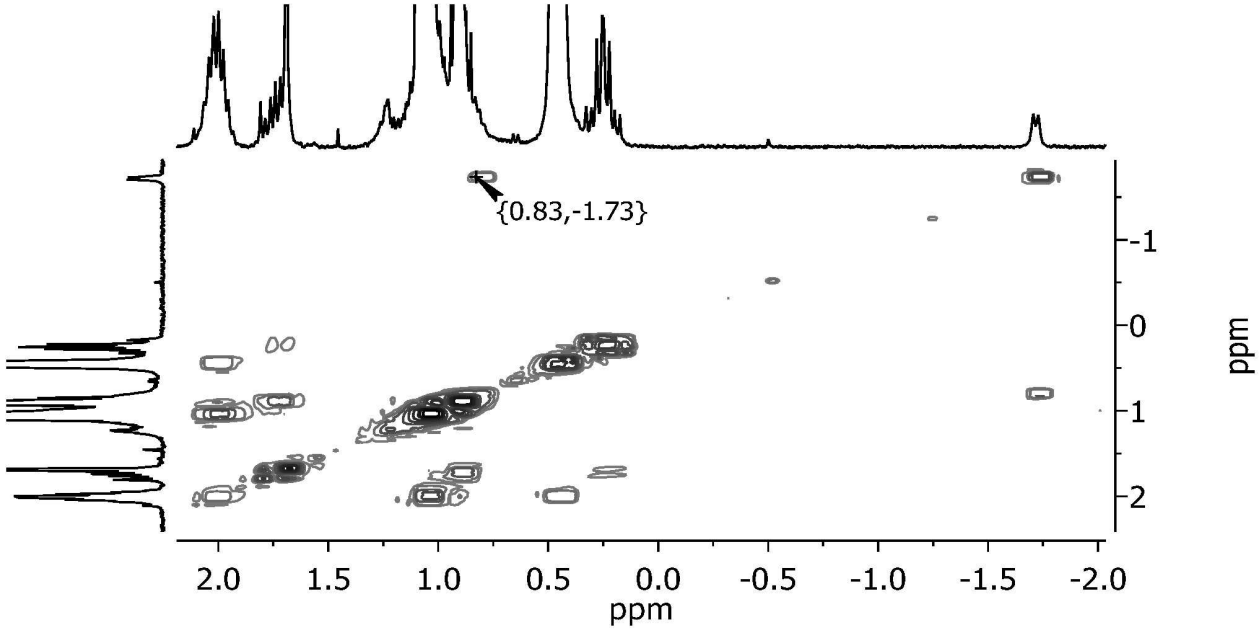

Figure S-4: gCOSY of sample in Figure S-3 showing location of central hydride resonance.

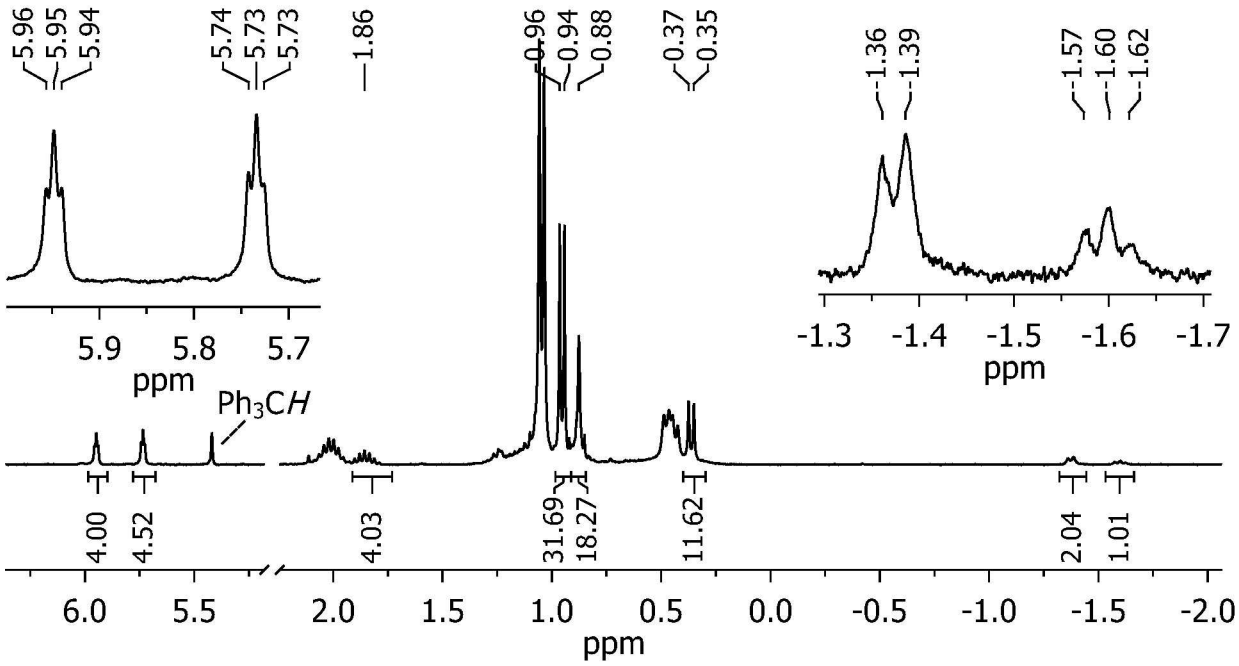

Figure S-5: ^{1}H NMR of 4.6 mM solution of $[Me_4C_2(C_5H_4)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of HAl^iBu_2.

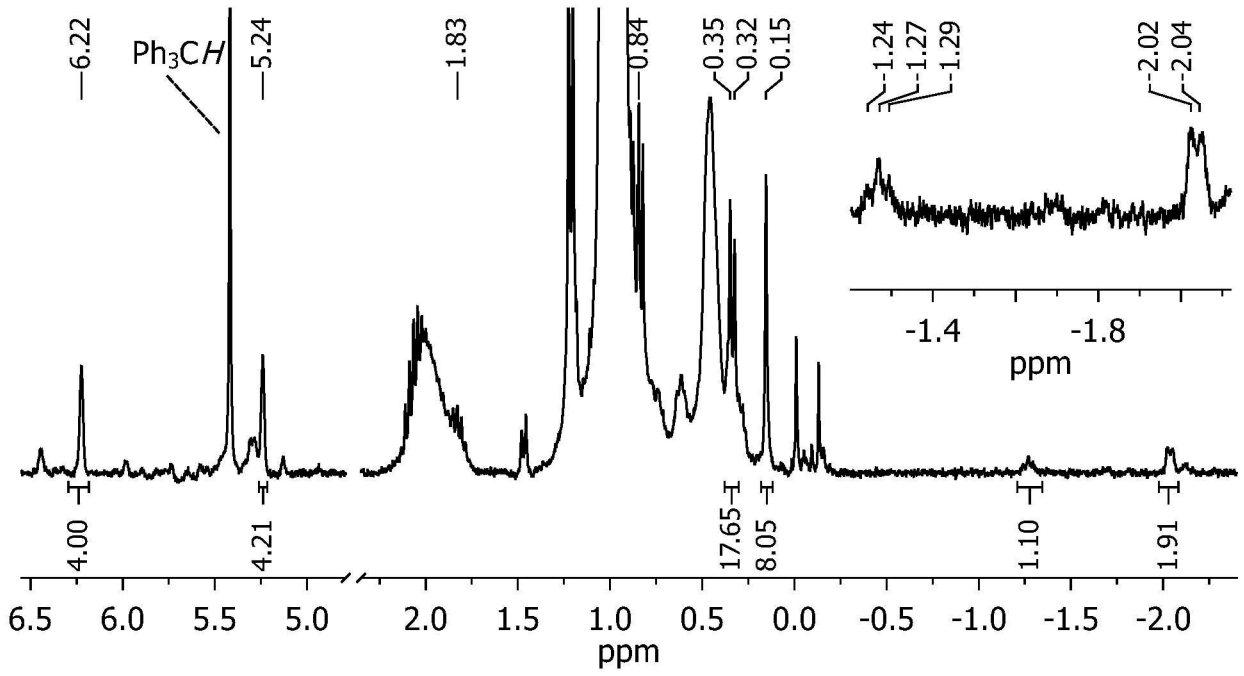

Figure S-6: ^{1}H NMR of 8.1 mM solution of $[Me_2Si(C_5H_4)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of HAl^iBu_2.

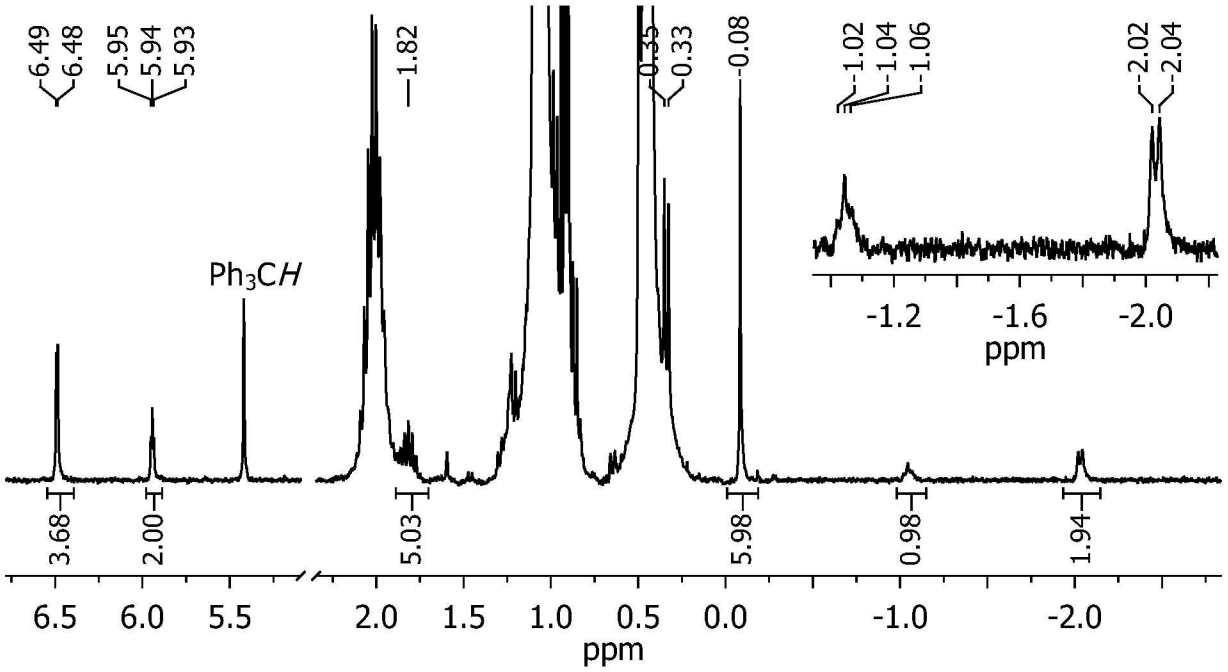

Figure S-7: ^{1}H NMR of 3.6 mM solution of $[(Me_2Si)_2(C_5H_3)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 10 equiv of HAl^iBu_2.

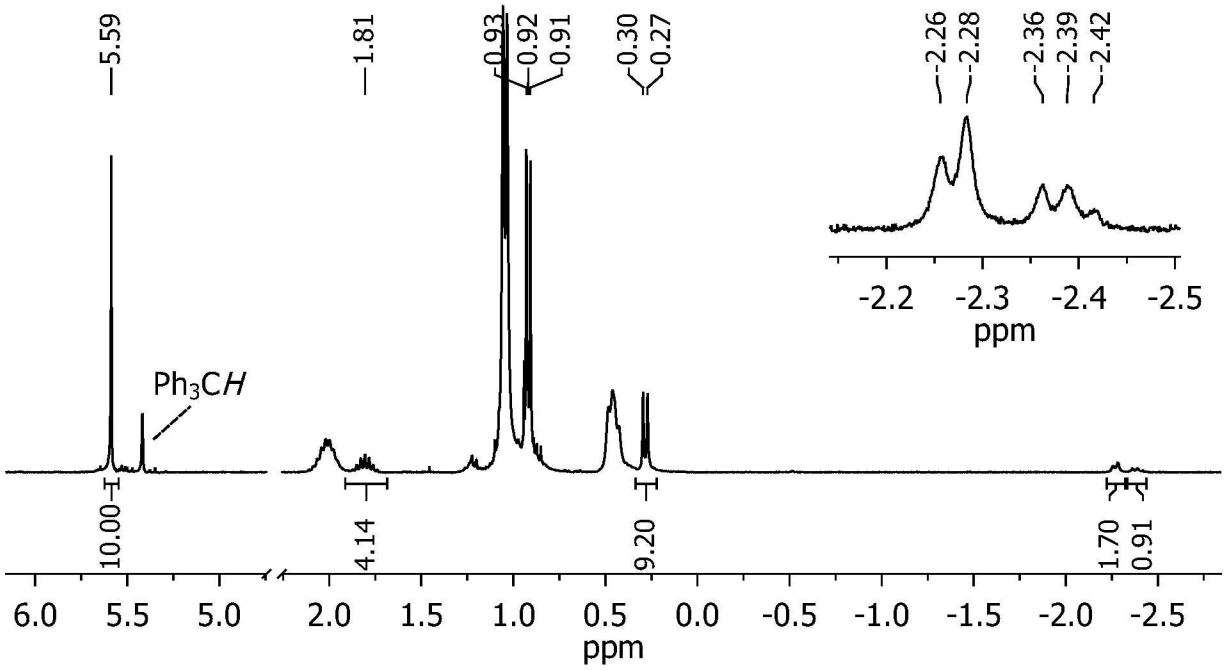

Figure S-8: ^{1}H NMR of 11 mM solution of $[(C_5H_5)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of HAl^iBu_2.

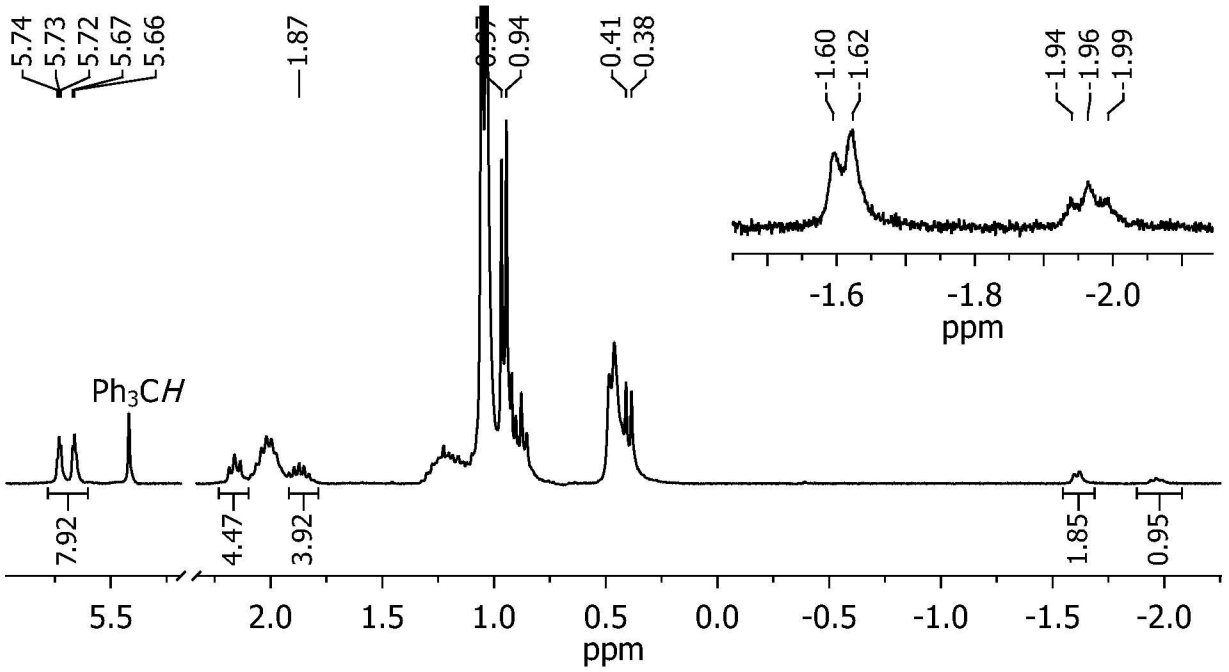

Figure S-9: ^{1}H NMR of 10 mM solution of $[(C_5H_4{}^{n}Bu)_2Zr(\mu\text{-}H)_3(Al{}^{i}Bu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of $HAl{}^{i}Bu_2$.

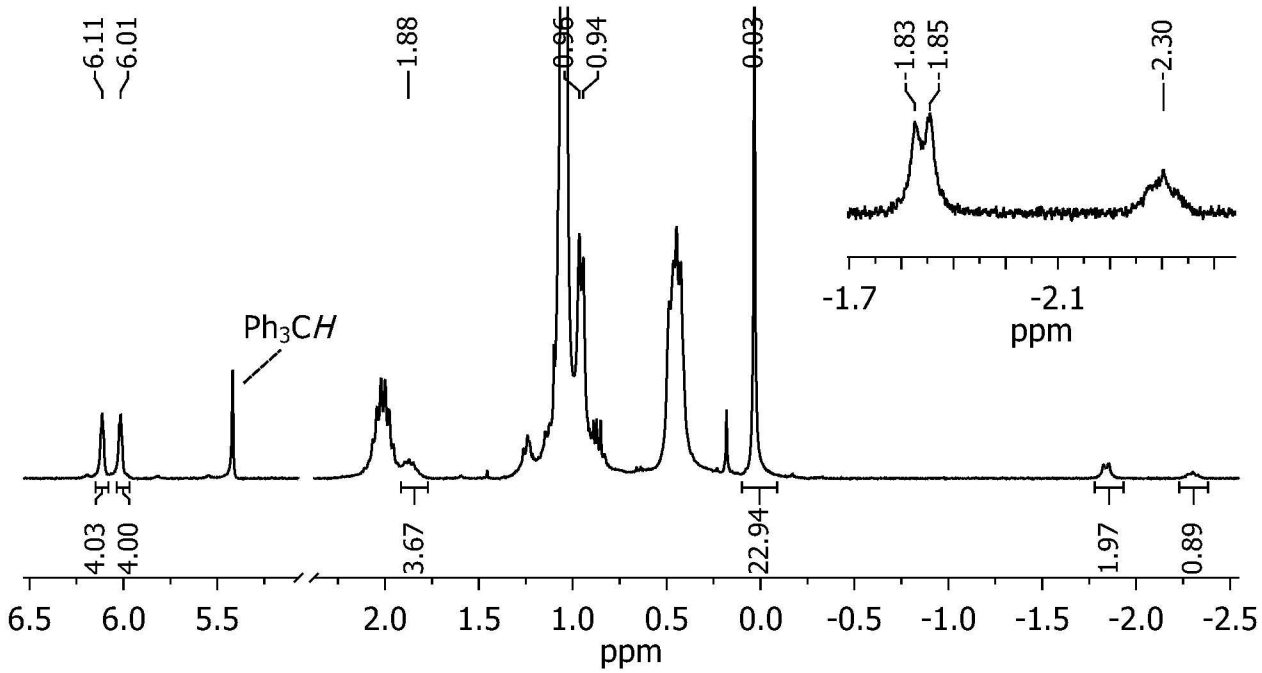

Figure S-10: ^{1}H NMR of 5.3 mM solution of $[(C_5H_4TMS)_2Zr(\mu\text{-}H)_3(Al{}^{i}Bu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of $HAl{}^{i}Bu_2$.

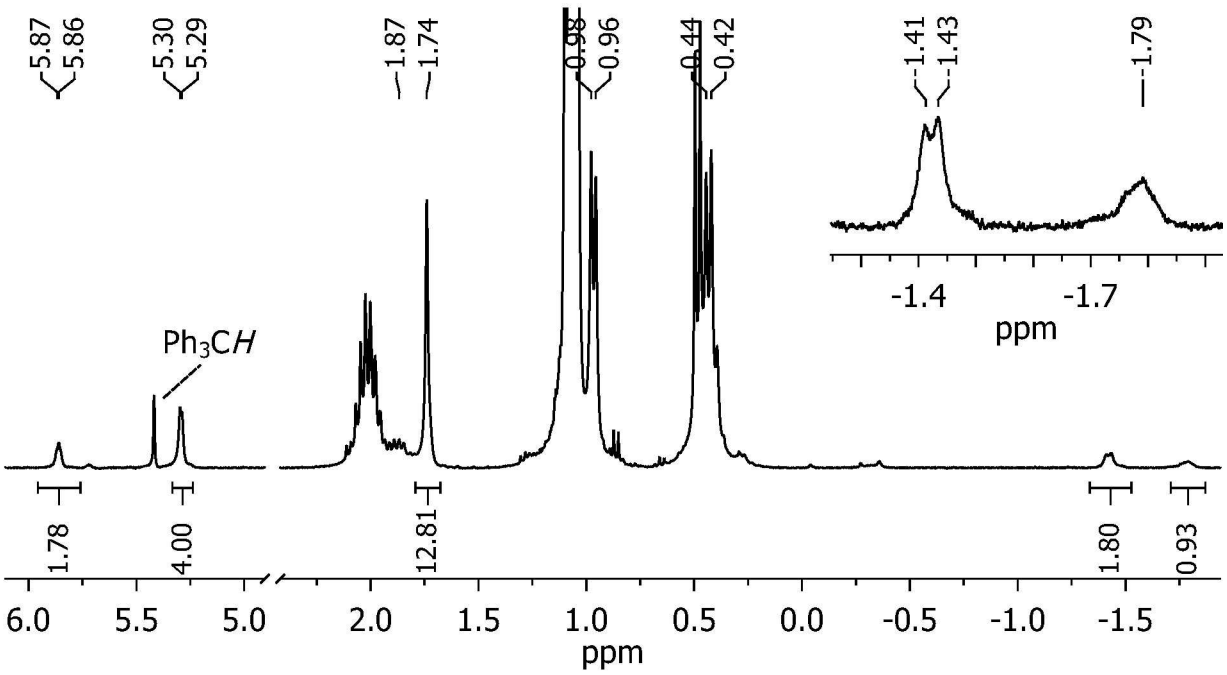

Figure S-11: ^{1}H NMR of 4.1 mM solution of $[(1,2\text{-}Me_2C_5H_3)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 10 equiv of HAl^iBu_2.

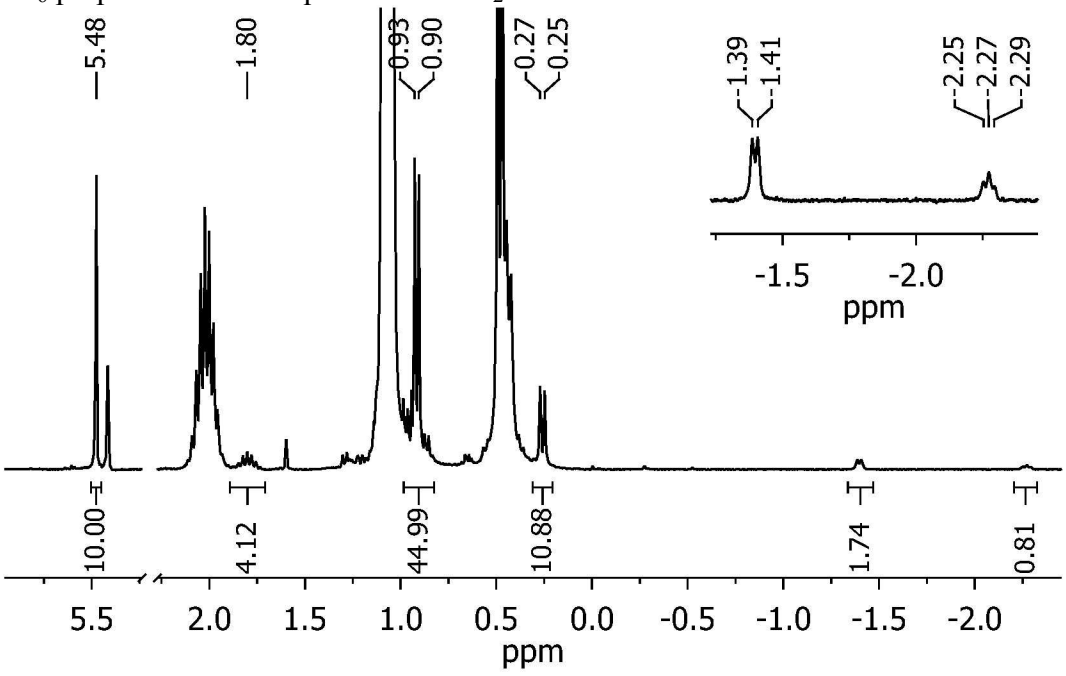

Figure S-12: ^{1}H NMR of 16 mM solution of $[(C_5H_5)_2Hf(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 5 equiv of HAl^iBu_2.

4. Evidence for Formation of $ClAl^iBu_2$ during synthesis of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$

Variable temperature spectra of a 3.1 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ in toluene-d_8 prepared as above show isobutyl-methyl resonances of $ClAl^iBu_2$ at 1.01 ppm ($^3J_{HH}$ = 7 Hz) at –25 ºC (Figure S-13). At other temperatures the peaks are not sufficiently resolved to definitively identify the signals of $ClAl^iBu_2$, however the overall shape of the peaks in the zirconocene spectra are consistent with this assignment.

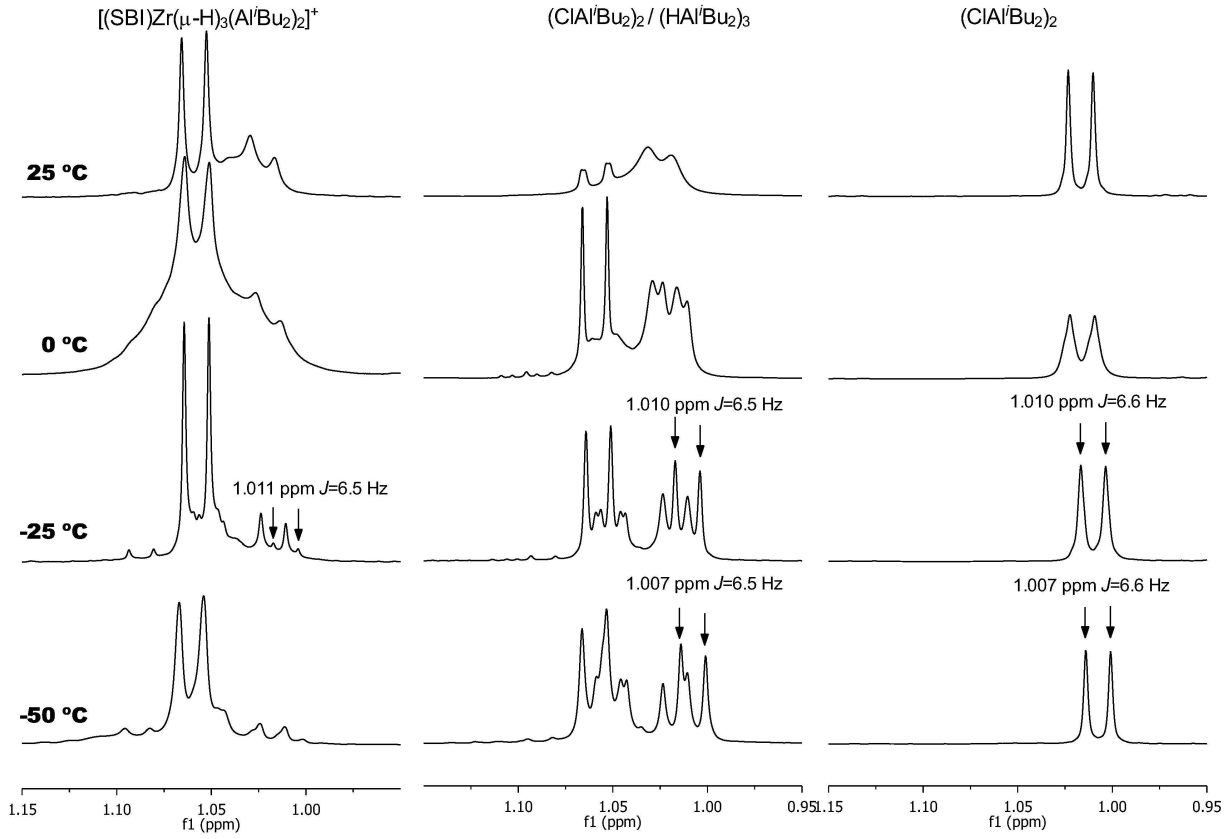

Figure S-13: Variable temperature ^1H NMR spectra of the ^{i}Bu-CH_3 signals of toluene-d_8 solutions of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ (3.1 mM), a 1:1 mix of HAl^iBu_2 and $ClAl^iBu_2$ (21 mM each) and pure $ClAl^iBu_2$ (42 mM).

5. EXSY of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$

A 3.1 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ was prepared as above and an EXSY spectrum with a mixing time of 300 ms was collected (Figure S-14). Crosspeaks between the Al-

H resonances for the three mixed HAl^iBu_2 / $ClAl^iBu_2$ clusters were visible as well as crosspeaks for free and bound isobutyl aluminum groups. No crosspeak was observed between free and complex-bound Al-H resonances.

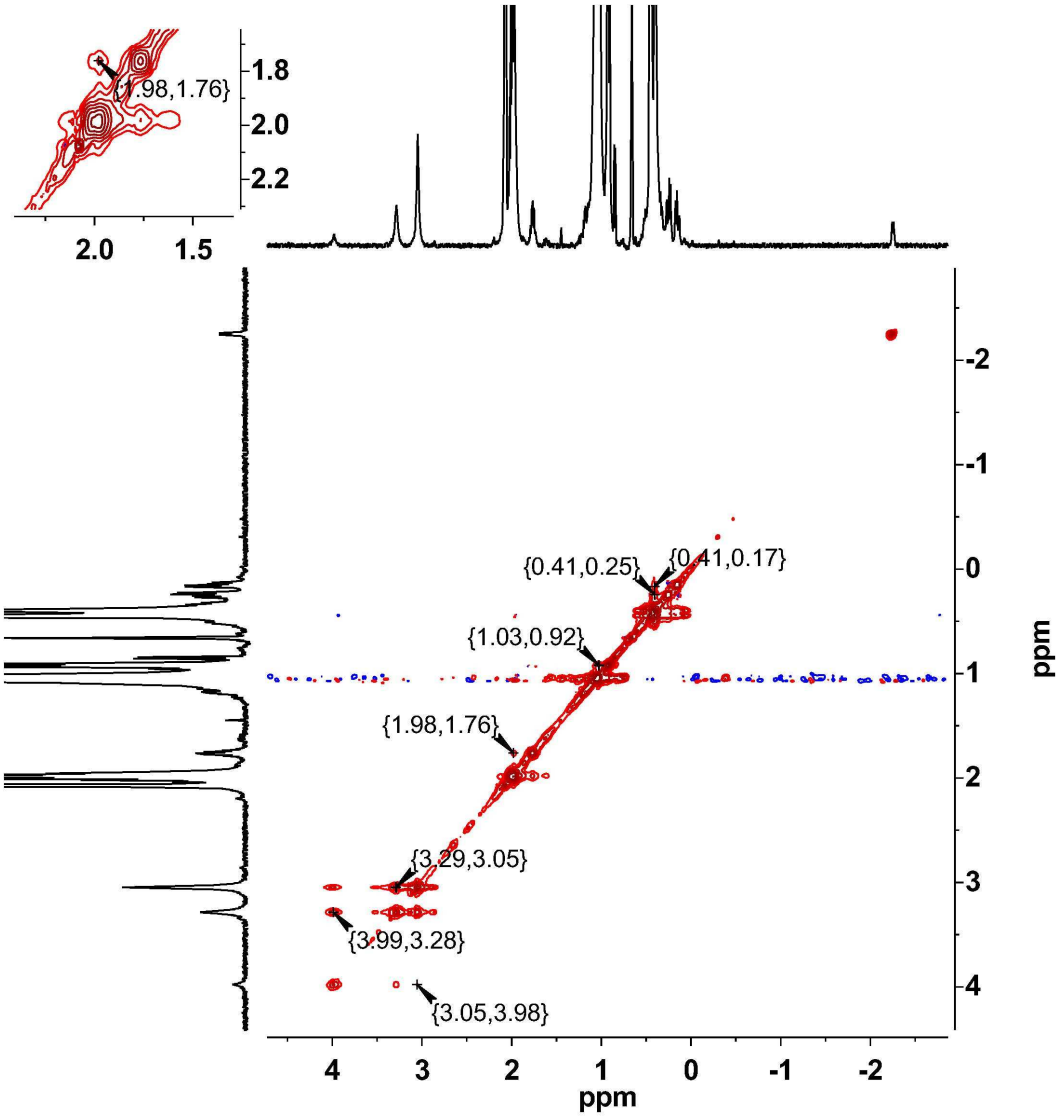

Figure S-14: EXSY spectrum of a 3.1 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ collected with a mixing time of 300 ms at 25 ºC. Inset shows expansion of isobutyl CH_3 resonances with crosspeak for free and bound species marked.

6. Synthesis of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$

In a glovebox 100.3 mg (0.2236 mmol) $(SBI)ZrCl_2$ and 205.8 mg (0.2231 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$ were weighed into a 25 mL round bottom flask. Approximately 15 mL of

toluene which had been vacuum transferred from titanocene was added resulting in an orange-red solution. 1.2 mL (6.7 mmol, 30 equiv) of $HAl^{i}Bu_2$ was syringed into the solution resulting in a green solution which faded to yellow upon stirring. A swivel frit with another 25 mL round-bottom flask was attached and the reaction vessel was taken to a high vacuum line. The reaction mixture was allowed to stir at room temperature for 30 minutes, following which toluene was removed *in vacuo* until no more liquid would come off, leaving 2-3 mL of a red solution. Approximately 10 mL of pentane was vacuum transferred from titanocene onto the reaction mixture. After stirring for one hour at room temperature a yellow precipitate was collected by filtration and washed twice with pentane. 128.0 mg (47% yield) of $[(SBI)Zr(\mu\text{-}H)_3(Al^{i}Bu_2)_2][B(C_6F_5)_4]$ was collected. ^1H NMR of the solid was indistinguishable with that formed *in situ* with the exception of the absence of peaks due to free $HAl^{i}Bu_2$ or $ClAl^{i}Bu_2$. Attempts to obtain elemental analysis of the compound were unsuccessful as the pale yellow solid was found to darken overnight at room temperature in a vacuum sealed ampoule. The solid could be stored for over one month at –40 ºC in a glovebox freezer suggesting that the low yield obtained in this reaction was due at least in part to the prolonged stirring at room temperature.

7. Reactions of zirconocene dichloride complexes with $HAlMe_2$ and $[Ph_3C][B(C_6F_5)_4]$.

Each zirconocene dichloride was weighed in a glove box into a 1-dram vial and a small quantity of $HAlMe_2$ was added to the vial. Then 0.7 mL of benzene-d_6 was added and the vial was capped and shaken to mix the reagents. The resulting solution was added to 1 equiv $[Ph_3C][B(C_6F_5)_4]$ in a second vial. The final solution of the title complex was transferred to a J-Young tube for NMR analysis.

$[$*rac*$\text{-}(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2][B(C_6F_5)_4]$. 1.0 mg (0.0022 mmol) *rac*-$Me_2Si(1\text{-indenyl})_2$ $ZrCl_2$, 1.4 mg (0.024 mmol, 11 equiv) $HAlMe_2$ and 2.1 mg (0.0023 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$.

^{1}H NMR (300 MHz, benzene-d_6) δ 6.70 (dd, $^3J_{HH}$ = 20, 8 Hz, 6H, Ar-H), 6.29 (d, $^3J_{HH}$ = 2 Hz, 2H, C_5-H), 5.40 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 0.62 (s, 6H, $Si(CH_3)_2$), -0.15 (m, Zr-H), -2.06 (d, $^2J_{HH}$ = 4 Hz, 2H, Zr-H_2).

[*rac*-(EBI)Zr(μ-H)$_3$(AlMe$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.8 mg (0.0043 mmol) *rac*-C_2H_4(1-indenyl)$_2$ $ZrCl_2$, 2.1 mg (0.036 mmol, 8 equiv) $HAlMe_2$ and 4.0 mg (0.0043 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.42 (d, $^3J_{HH}$ = 9 Hz, 3H, Ar-H), 6.88 (dd, $^3J_{HH}$ = 21, 9 Hz, 7H, Ar-H), 6.64 (m, 2H, Ar-H), 5.60 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 5.49 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 1.36 (s, 4H, C_2H_4), -1.00 (br, 1H, Zr-H), -1.45 (d, $^3J_{HH}$ = 9 Hz, 2H, Zr-H_2).

[*rac*-(EBTHI)Zr(μ-H)$_3$(AlMe$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 2.0 mg (0.0046 mmol) *rac*-C_2H_4(4,5,6,7-tetrahydro-1-indenyl)$_2ZrCl_2$, 2.2 mg (0.038 mmol, 8 equiv) $HAlMe_2$ and 4.2 mg (0.0046 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.70 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 5.15 (d, $^3J_{HH}$ = 3 Hz, 2H, C_5-H), 2.50 (m, 3H), 2.17 (m, 6H), 1.41 (m, 6H), -0.94 (s, 2H, Zr-H_2).

[Me$_2$Si(C$_5$H$_4$)$_2$Zr(μ-H)$_3$(AlMe$_2$)$_2$][B(C$_6$F$_5$)$_4$]. 1.8 mg (0.0052 mmol) *rac*-$Me_2Si(C_5H_4)_2$ $ZrCl_2$, 2.4 mg (0.041 mmol, 8 equiv) $HAlMe_2$ and 4.8 mg (0.0052 mmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.91 (pt, $^3J_{HH}$ = 2 Hz, 4H, C_5-H), 5.13 (pt, $^3J_{HH}$ = 2 Hz, 4H, C_5-H), 0.21 (s, 6H, $Si(CH_3)_2$), -1.61 (t, $^2J_{HH}$ = 9 Hz, 1H, Zr-H), -2.93 (d, $^2J_{HH}$ = 7 Hz, 2H, Zr-H_2).

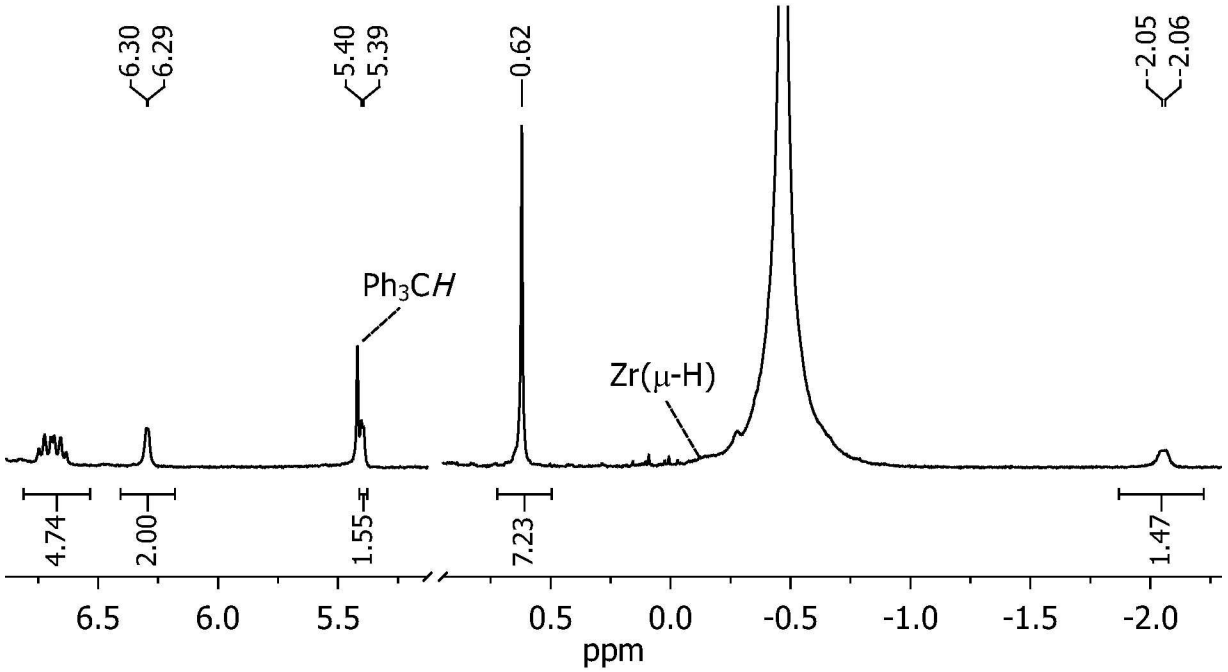

Figure S-15: ^{1}H NMR of 3.2 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 6 equiv of $HAlMe_2$.

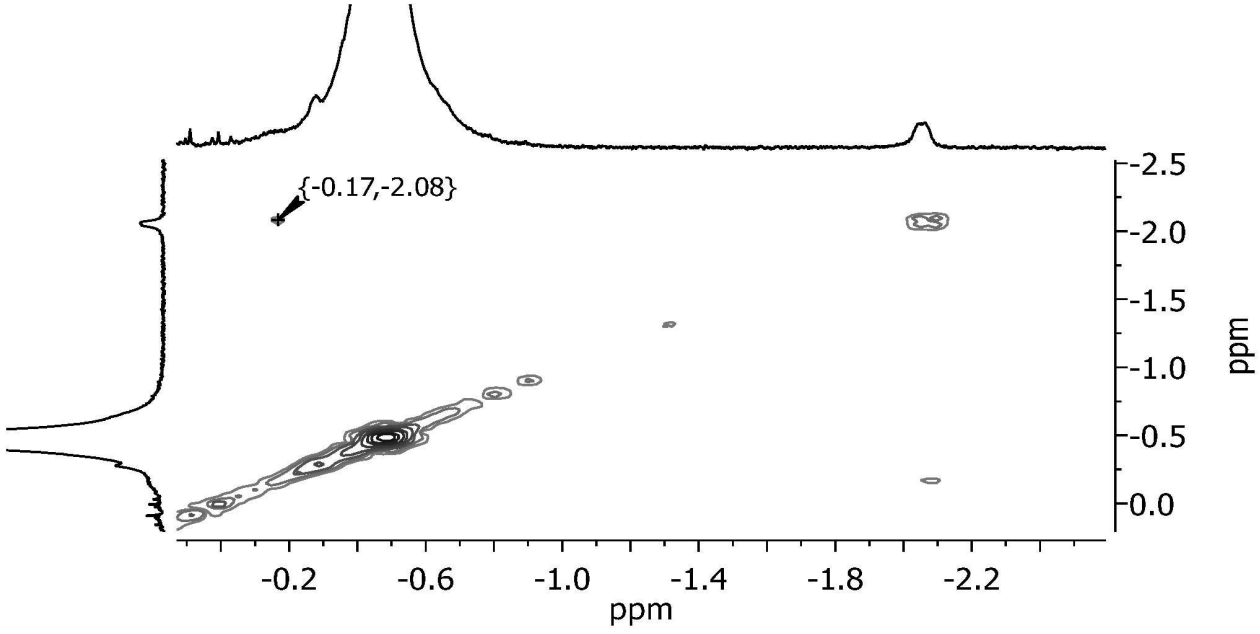

Figure S-16: gCOSY of sample from Figure S-15.

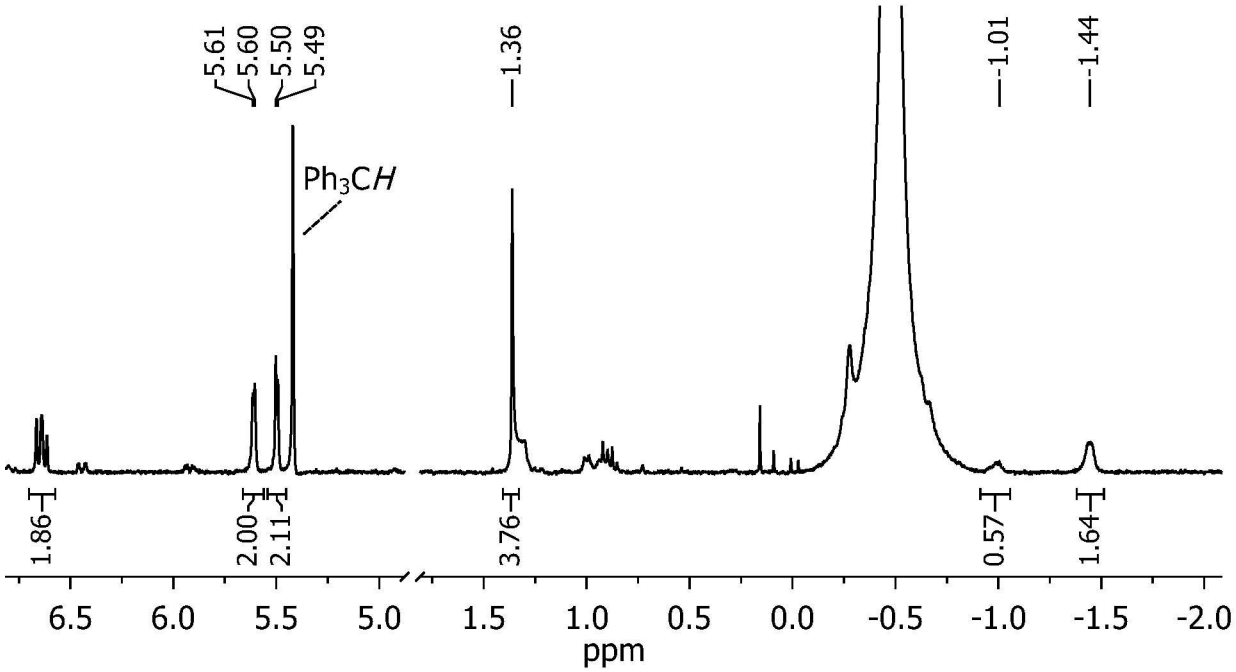

Figure S-17: ^{1}H NMR of 6.1 mM solution of [(EBI)Zr(μ-H)$_3$(AlMe$_2$)$_2$][B(C$_6$F$_5$)$_4$] in benzene-d_6 prepared with 8.4 equiv of HAlMe$_2$.

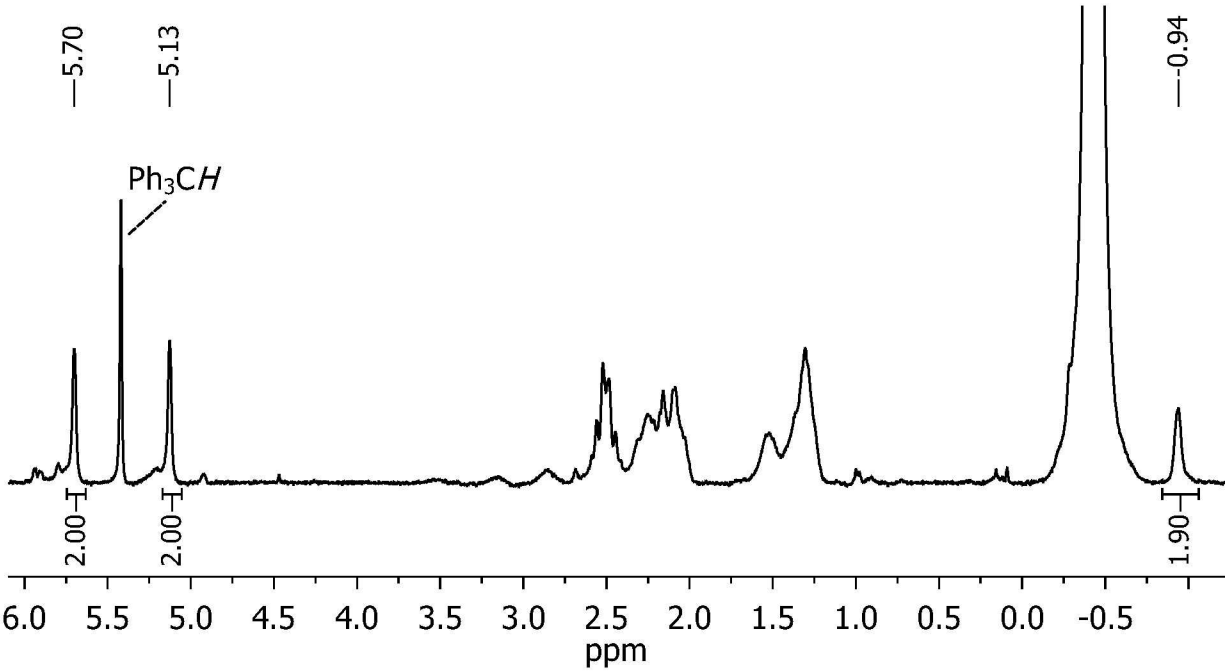

Figure S-18: ^{1}H NMR of 6.6 mM solution of [(EBTHI)Zr(μ-H)$_3$(AlMe$_2$)$_2$][B(C$_6$F$_5$)$_4$] in benzene-d_6 prepared with 8.1 equiv of HAlMe$_2$.

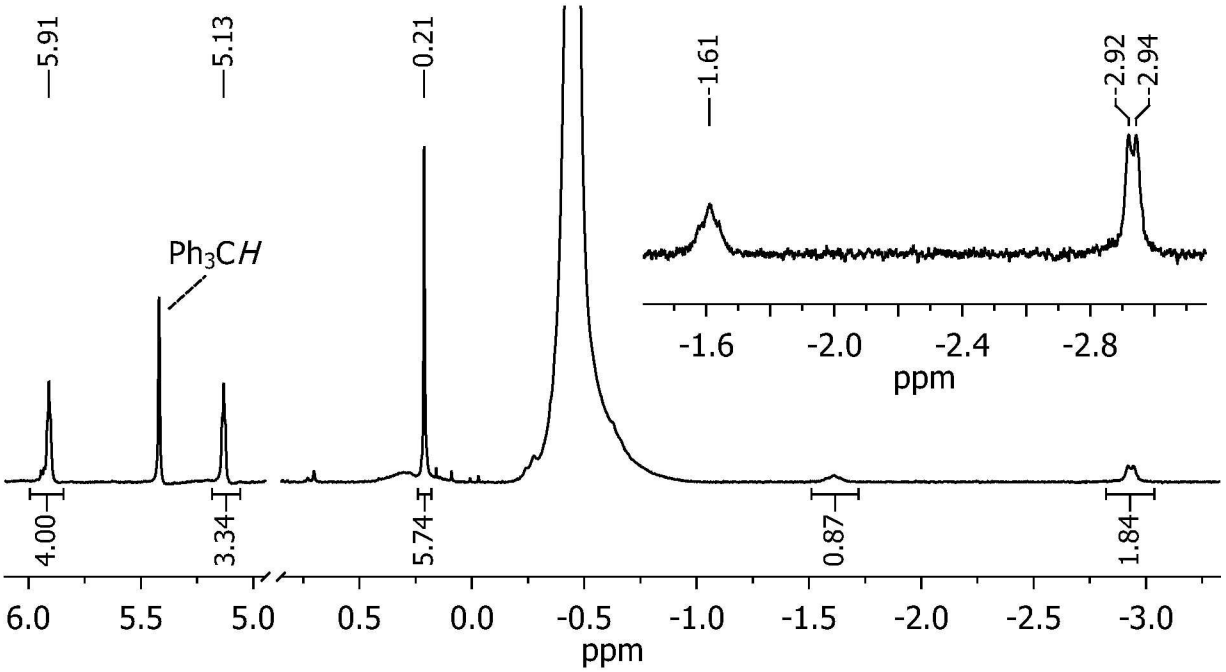

Figure S-19: ^{1}H NMR of 4.1 mM solution of $[Me_2Si(C_5H_4)Zr(\mu\text{-}H)_3(AlMe_2)_2][B(C_6F_5)_4]$ in benzene-d_6 prepared with 7.9 equiv of $HAlMe_2$.

8. ^{1}H NMR of $[(SBI)Zr(\mu\text{-}H)_3(AlMe_x{}^i Bu_{2-x})_2][B(C_6F_5)_4]$

The title complexes were prepared from a 3 mM solution of $[(SBI)Zr(\mu\text{-}H)_3)(Al^iBu_2)_2]^+$ prepared as above with 5 equiv of HAl^iBu_2 and then adding $^1/_3$, 1, 2 or 3 equiv of $AlMe_3$ to the NMR tube via microliter syringe. Shaking the sealed tube and collecting ^{1}H NMR spectra yielded the spectra shown in Figure 6 of the text.

To test the reversibility of this reaction, 1.2 mg $(SBI)ZrMe_2$ (0.0029 mmol) was dissolved in 0.7 mL benzene-d_6 and added to 2.5 mg $[Ph_3C][B(C_6F_5)_4]$ to give an orange cloudy solution of $[(SBI)ZrMe]^+$. 2.6 μL HAl^iBu_2 (0.015 mmol, 5 equiv) was then syringed in. Immediate ^{1}H NMR showed the presence of $[(SBI)Zr(\mu\text{-}H)_3)(Al^iBu_2)_2]^+$ which after stirring for 2 hours became the dominant species (Figure S-20).

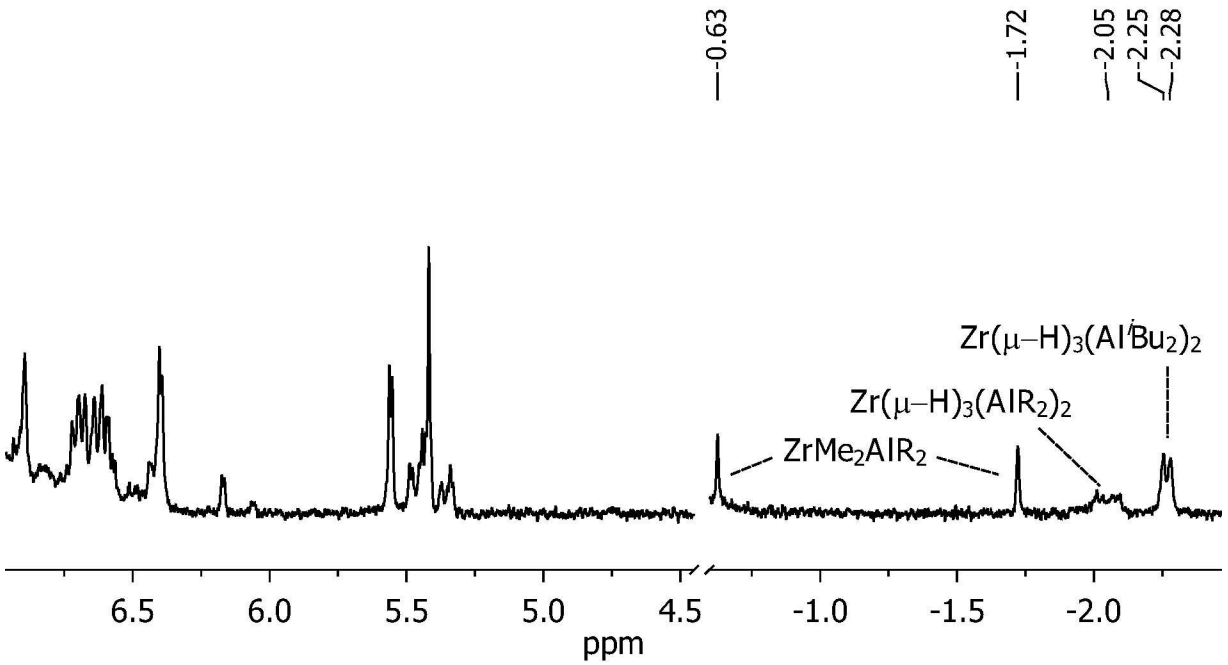

Figure S-20: ^{1}H NMR of 4.1 mM solution of [(SBI)Zr(μ-H)$_3$(AlMe$_x$^{i}Bu$_{2-x}$)$_2$][B(C$_6$F$_5$)$_4$] in benzene-d_6 prepared from [(SBI)ZrMe]$^+$ with 5.0 equiv of HAl^{i}Bu$_2$.

9. gCOSY of [(SBI)Zr(μ-H)$_3$(AlMe$_x$^{i}Bu$_{2-x}$)$_2$][Me-MAO]$^-$

A 1.9 mM solution of [(SBI)Zr(μ-H)$_3$(AlMe$_x$^{i}Bu$_{2-x}$)$_2$][Me-MAO]$^-$ was prepared by first adding 50.6 mg MAO, which had been dried under vacuum at 50 ºC for 3 hours, to a 20 mL vial in the glove box. 3.5 mL of benzene-d_6 was then added and the mixture was stirred to dissolve as much MAO as possible. The mixture was allowed to sit undisturbed for 30 minutes after which time 3 mL of MAO solution was pipetted off leaving behind a gel. 2.6 mg of (SBI)ZrCl$_2$ (0.0058 mmol) was then added to the solution to give an orange solution containing [(SBI)ZrMe$_2$AlMe$_2$]$^+$ and [(SBI)ZrMe$^{+\cdots}$MeMAO$^-$]. 0.7 mL of this solution was transferred to a J Young tube and 15 μL HAl^{i}Bu$_2$ was added neat via microliter syringe. A gCOSY spectrum (Figure S-21) was obtained which showed coupling of the Zr(μ-H)$_2$ peak to a downfield peak at 0.58 ppm consistent with the central Zr(μ-H).

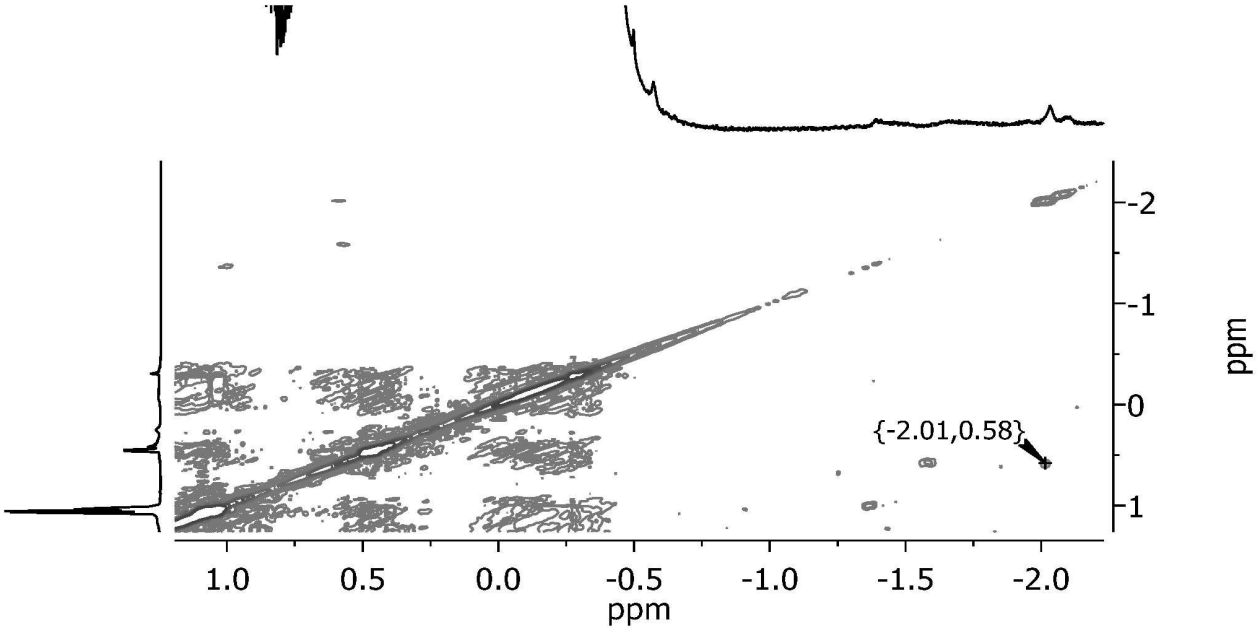

Figure S-21: gCOSY of a solution of $[(SBI)Zr(\mu\text{-}H)_3(AlMe_x{}^iBu_{2-x})_2][MeMAO]^-$ showing coupling between hydride signals.

10. ^{1}H NMR spectrum of the dichloro-bridged cation $[(SBI)Zr(\mu\text{-}Cl)_2Al{}^iBu_2]^+$

(Method 1A: $HAl{}^iBu_2$ / $ClAl{}^iBu_2$) 1.0 mg $(SBI)ZrCl_2$ (2.2 μmol) and 2.1 mg $[Ph_3C][B(C_6F_5)_4]$ (2.3 μmol, 1 equiv) were added to a 1-dram vial in the glove box. 0.7 mL benzene-d_6 was added. 0.4 μL $HAl{}^iBu_2$ (2 μmol, 1 equiv) and 0.4 μL $ClAl{}^iBu_2$ (2 μmol, 1 equiv) were added neat via microliter syringe. The mixture was shaken to yield a blue solution with blue oil. The mixture was transferred to a J-Young NMR tube and spectra were obtained (Figure S-22).

(Method 1B: $HAl{}^iBu_2$ / $ClAl{}^iBu_2$) The same species can be formed by first making the hydride cation, $[(SBI)Zr(\mu\text{-}H)_3(Al{}^iBu_2)_2][B(C_6F_5)_4]$, and then adding an excess of $ClAl{}^iBu_2$. 1.0 mg $(SBI)ZrCl_2$ (2.2 μmol) and 4.0 μL $HAl{}^iBu_2$ (22 μmol, 10 equiv) along with 0.7 mL benzene-d_6 were added to a 1-dram vial in the glove box. The resulting solution was added to a second vial containing 2.2 mg $[Ph_3C][B(C_6F_5)_4]$ (2.4 μmol, 1 equiv) resulting in a solution of the hydride cation. 8.0 μL of neat $ClAl{}^iBu_2$ (41 μmol, 19 equiv) was then added via microliter syringe. The

mixture was shaken to yield a blue solution. The mixture was transferred to a J-Young NMR tube and spectra were obtained (Figure S-22).

(Method 2: Et_3Si^+) In the glove box, a slurry of 2.1 mg (SBI)$ZrCl_2$ (4.7 μmol) was formed in a solution containing 4.3 mg (4.7 μmol, 1 equiv) of $[Ph_3C][B(C_6F_5)_4]$ in 0.7 mL benzene-d_6. The slurry was added to a J-Young tube and 0.9 μL ClAl^iBu_2 (5 μmol, 1 equiv) was added to the side of the tube without mixing. The sample was removed from the box, frozen and the head space was evacuated on the high-vacuum line. 0.04 mL Et_3SiH (300 μmol, 64 equiv) was vacuum-transferred in from a storage flask containing CaH_2. Upon thawing and mixing a blue solution and blue oil formed. The sample was pumped down to remove excess Et_3SiH and then redissolved in benzene-d_6. Spectra similar to those from Method A were obtained (Figure S-24).

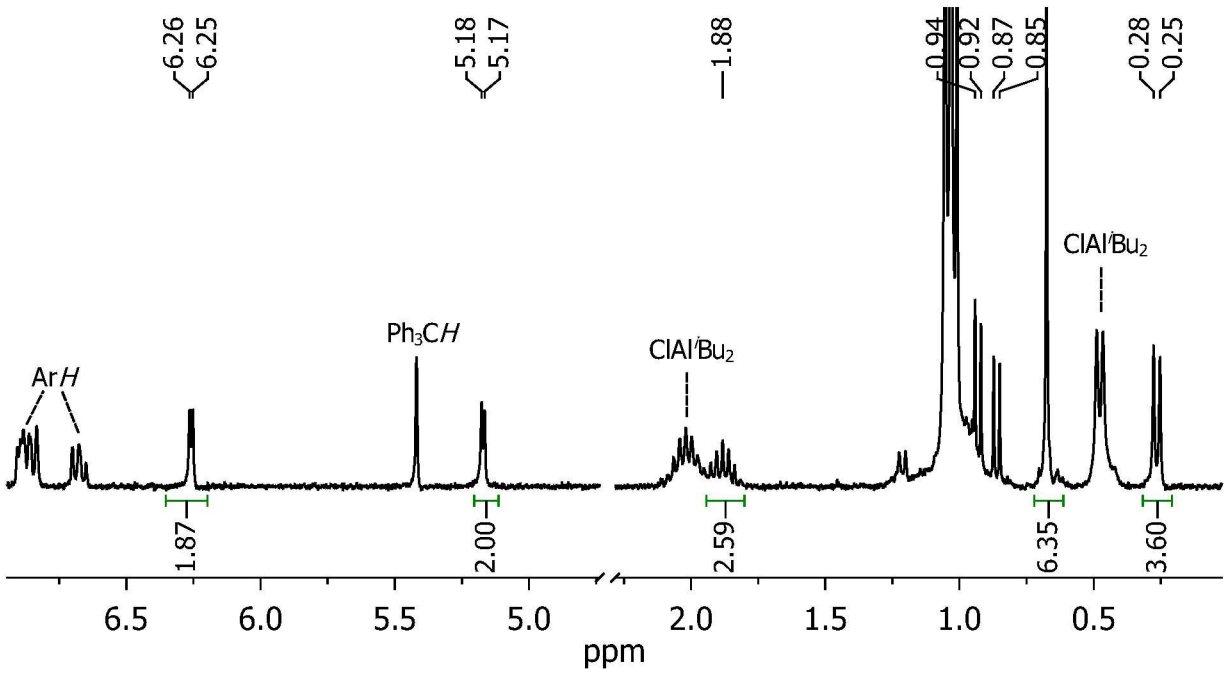

Figure S-22: ^{1}H NMR spectrum of $[(SBI)Zr(\mu\text{-}Cl)_2(Al^iBu_2)]^+$ formed from reaction with 1 equiv HAl^iBu_2 and 1 equiv ClAl^iBu_2.

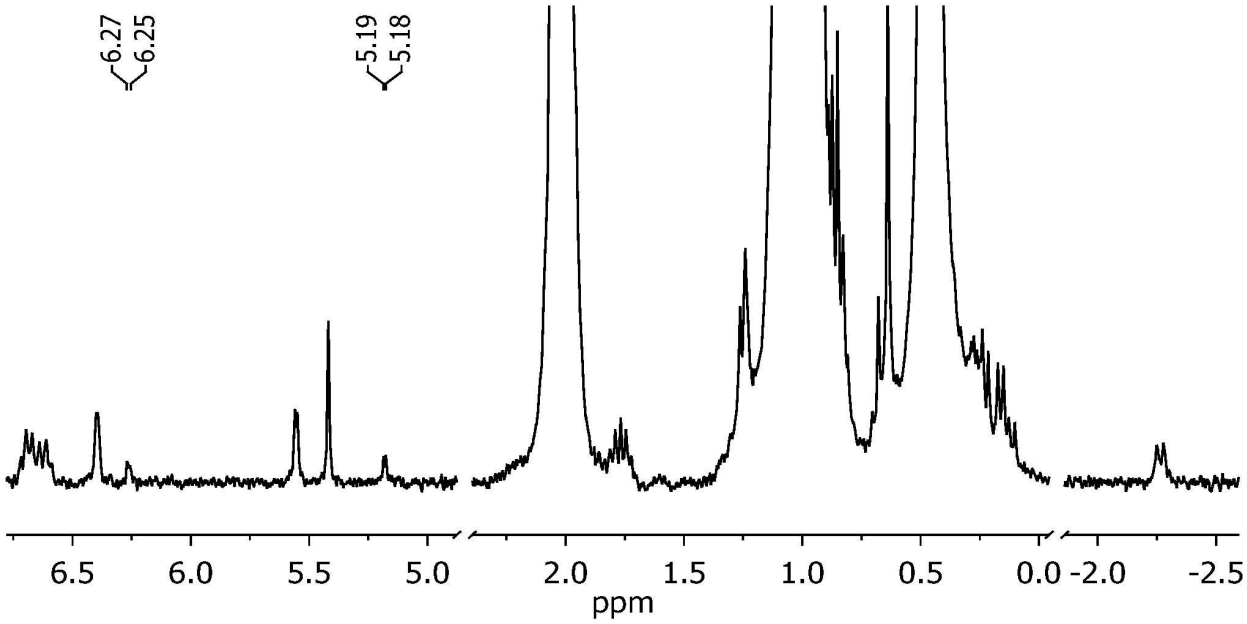

Figure S-23: ^{1}H NMR spectrum of $[(SBI)Zr(\mu\text{-}Cl)_2(Al^{i}Bu_2)]^{+}$ formed as a minor component from reaction of $[(SBI)Zr(\mu\text{-}H)_2(Al^{i}Bu_2)_2]^{+}$ (major component) with 18 equiv $ClAl^{i}Bu_2$.

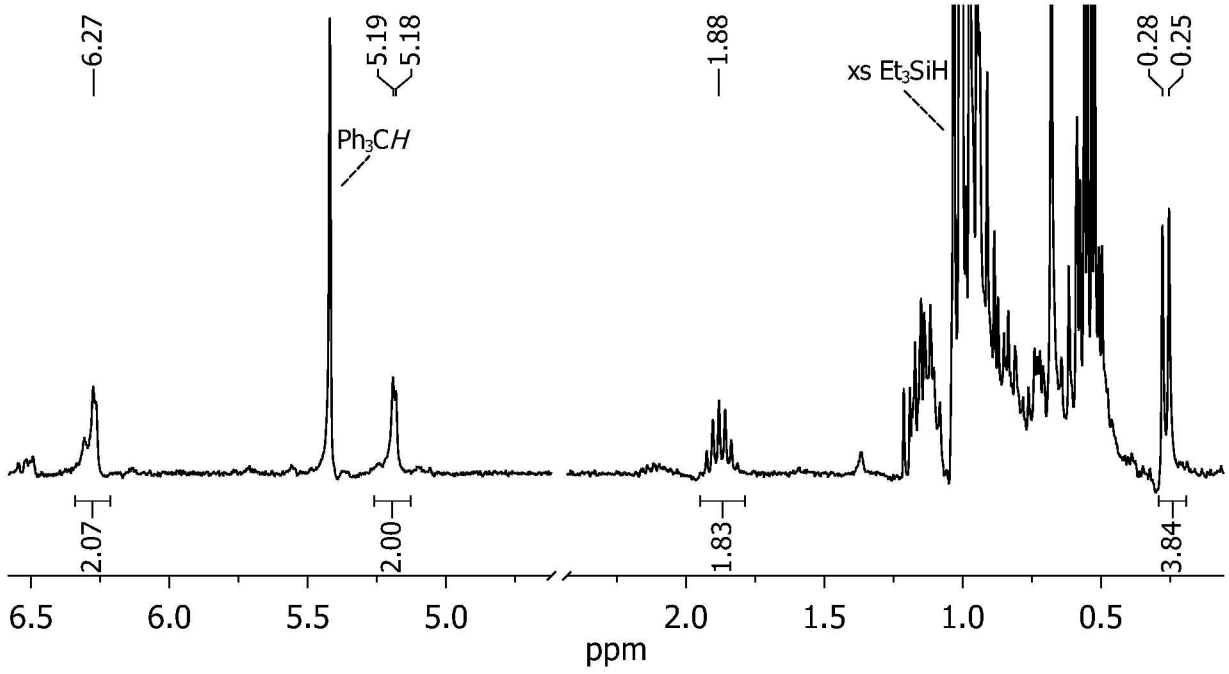

Figure S-24: ^{1}H NMR spectrum of $[(SBI)Zr(\mu\text{-}Cl)_2(Al^{i}Bu_2)]^{+}$ formed from reaction with 1 equiv $[Et_3Si]^{+}$ formed in situ and 1 equiv $ClAl^{i}Bu_2$.

11. ^{1}H NMR spectrum of the dichloro-bridged cation $[(SBI)Zr(\mu\text{-}Cl)_2AlMe_2]^+$

1.0 mg $(SBI)ZrMe_2$ (2.5 μmol) and 1.0 mg $AlCl_3$ (7.5 μmol, 3 equiv) were weighed into a 1-dram vial. 1.4 μL (15 μmol, 6 equiv) $AlMe_3$ was syringed onto the side of the vial. 2.3 mg (2.5 μmol, 1 equiv) $[Ph_3C][B(C_6F_5)_4]$ was weighed into a second 1-dram vial and was dissolved in 0.7 mL benzene-d_6. The $[Ph_3C]^+$ solution was added to the vial containing the zirconocene and mixed thoroughly to give a green solution which turned blue over the course of a few minutes. The solution was transferred to a J-Young tube for NMR analysis (Figure S-25).

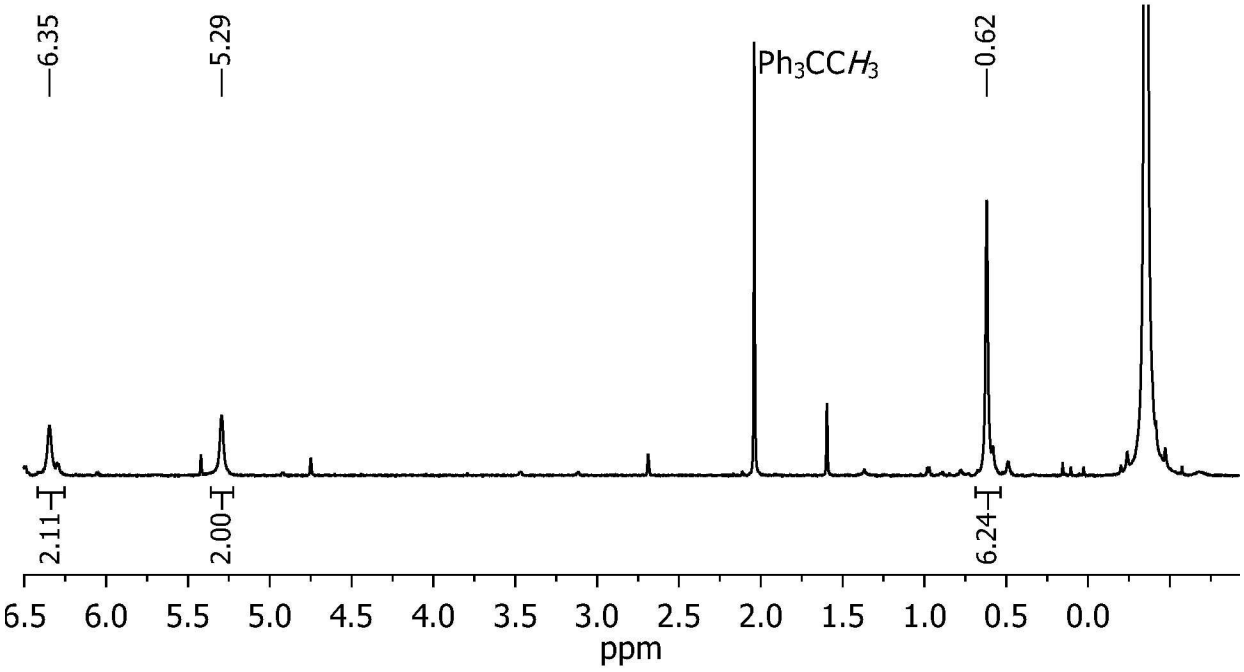

Figure S-25: ^{1}H NMR spectrum of a 3.6 mM solution of $[(SBI)Zr(\mu\text{-}Cl)_2(AlMe_2)]^+$.

12. UV-vis spectra of $[(SBI)Zr(\mu\text{-}Cl)_2(Al^iBu_2)]^+$

A 2.79 mM stock solution of $(SBI)ZrCl(\mu\text{-}H)_2(Al^iBu_2)$ was prepared by dissolving 12.5 mg $(SBI)ZrCl_2$ (27.9 μmol) in 10.0 mL toluene, vacuum-transferred from titanocene, to which was added 14.9 μL HAl^iBu_2 (83.6 μmol, 3.00 equiv). A 2.79 mM stock solution of $[Ph_3C][B(C_6F_5)_4]$ was likewise prepared by dissolving 25.7 mg of $[Ph_3C][B(C_6F_5)_4]$ in 10.0 mL toluene. For each UV-vis experiment 2.00 mL of each solution was combined and diluted to a volume of 10.0 mL

to afford a 0.558 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ to which was then added an additional amount of neat HAl^iBu_2 to afford solutions containing 3, 4, 5 or 10 equiv of HAl^iBu_2. Following measurement of the UV-vis spectrum of each sample (Figure 5 of the text) enough HAl^iBu_2 was added to reach 10 equiv relative to Zr. All samples afforded the same final spectrum regardless of how many equiv of HAl^iBu_2 were initially added.

To show the reversible nature of this equilibrium, successive 2.2 μL aliquots of $ClAl^iBu_2$ (11 μmol, 2.0 equiv) were added to one of the final samples containing 10 equiv HAl^iBu_2, collecting UV-vis spectra between each addition (Figure S-26).

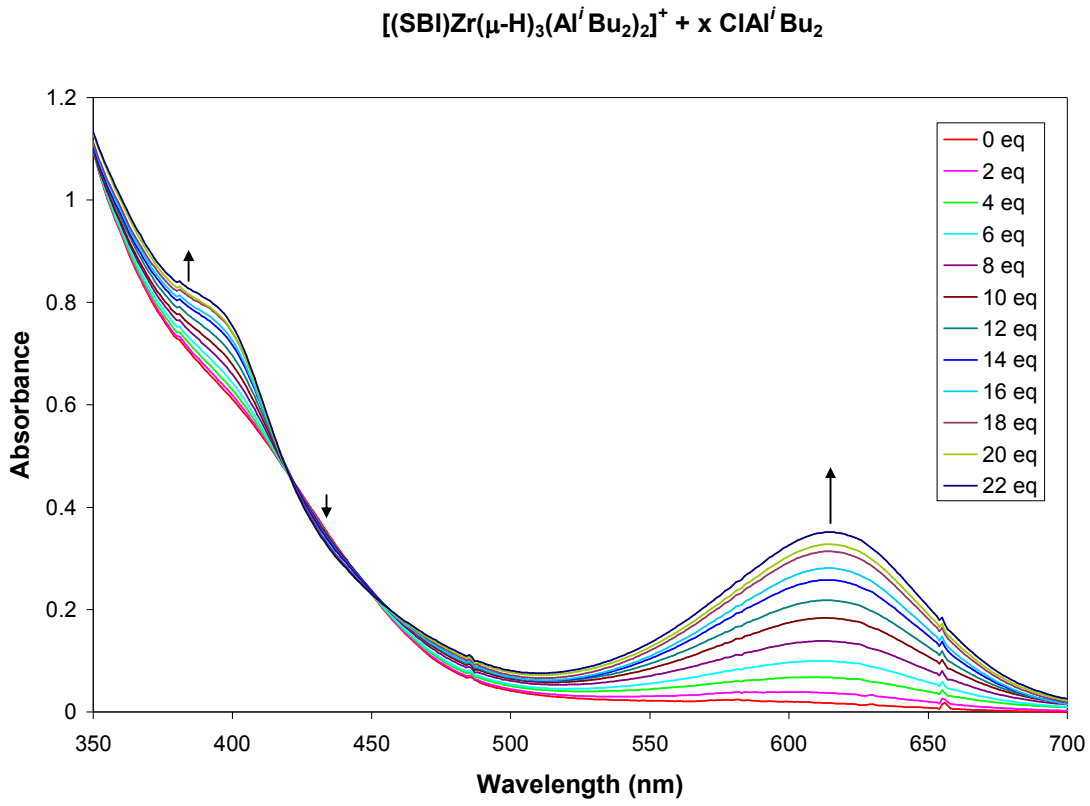

Figure S-26: UV-vis spectra of a 2.79 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ made with 10 equiv HAl^iBu_2 upon successive additions of 2 equiv $ClAl^iBu_2$.

13. Synthesis of $[\{(SBI)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$

In a glove box, 103.6 mg (SBI)$ZrCl_2$ (231.0 mmol) and 213 mg (230.9 mmol, 1 equiv) $[Ph_3C][B(C_6F_5)_4]$ were weighed into a 25 mL round bottom. A swivel frit and a second 25 mL round bottom were attached and 10 mL of toluene was added. The solution was degassed and 0.35 mL Et_3SiH was vacuum-transferred in at –78 ºC from a storage flask containing CaH_2. The solution was allowed to warm to room temperature giving a green solution and a green oil. After stirring for 30 minutes the solvent was removed *in vacuo* and 10 mL pentane was vacuum-transferred in from a titanocene-containing storage flask. After stirring for 5 minutes the reaction was filtered to give a green powder which was rinsed 3 times with pentane. 243.0 mg (96% yield) green powder was collected from the frit. $[\{(SBI)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ was found to be completely insoluble in benzene, toluene, bromobenzene or a 1:1 mixture of toluene and 1,2-difluorobenzene. Attempts to dissolve it in dichloromethane resulted in decomposition even at –70 ºC. Upon exposure to air the green solid was found to rapidly change to a bright red color.

Addition of 3.6 μL (18 μmol, 10 equiv) of $ClAl^iBu_2$ to a slurry of 4.0 mg (1.8 μmol) of $[\{(SBI)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ in 0.7 mL benzene-d_6 followed by sonication and stirring overnight resulted in the spectrum shown in Figure S-27, which is closely similar to that shown in Figure S-24. In the absence of $ClAl^iBu_2$ sonication and stirring $[\{(SBI)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ overnight in benzene-d_6 did not yield any C_5-*H* ^{1}H NMR signals.

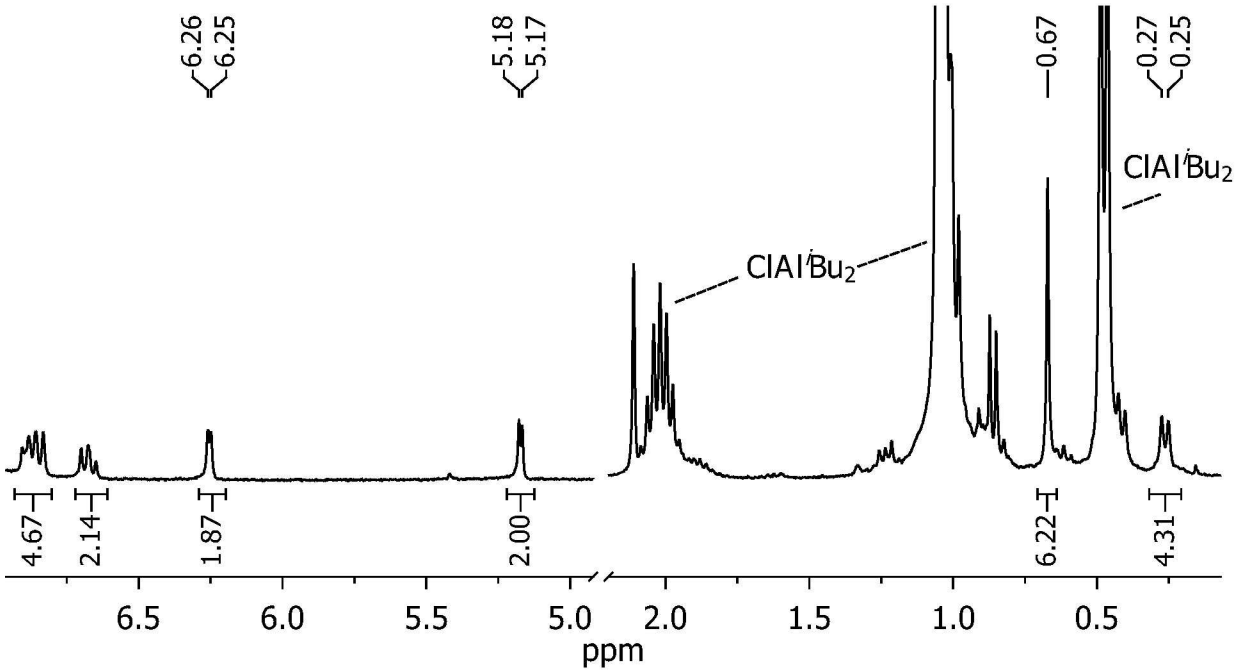

Figure S-27: ^{1}H NMR spectrum of $[(SBI)Zr(\mu\text{-}Cl)_2(Al^iBu_2)]^+$ formed from reaction of $[\{(SBI)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ with 10 equiv $ClAl^iBu_2$.

14. ^{1}H NMR spectrum of the cation $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$ with R = n-octyl

A measured amount of $AlOct_3$ solution in hexanes (25% by weight) was added to a J-Young tube via microliter syringe in the glovebox. The tube was evacuated for a minimum of 30 minutes to remove the hexanes. To this was then added a 3 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2][B(C_6F_5)_4]$ prepared as above. ^{1}H-NMR spectra were collected with various ratios of $AlOct_3$ to HAl^iBu_2 (Figure S-28).

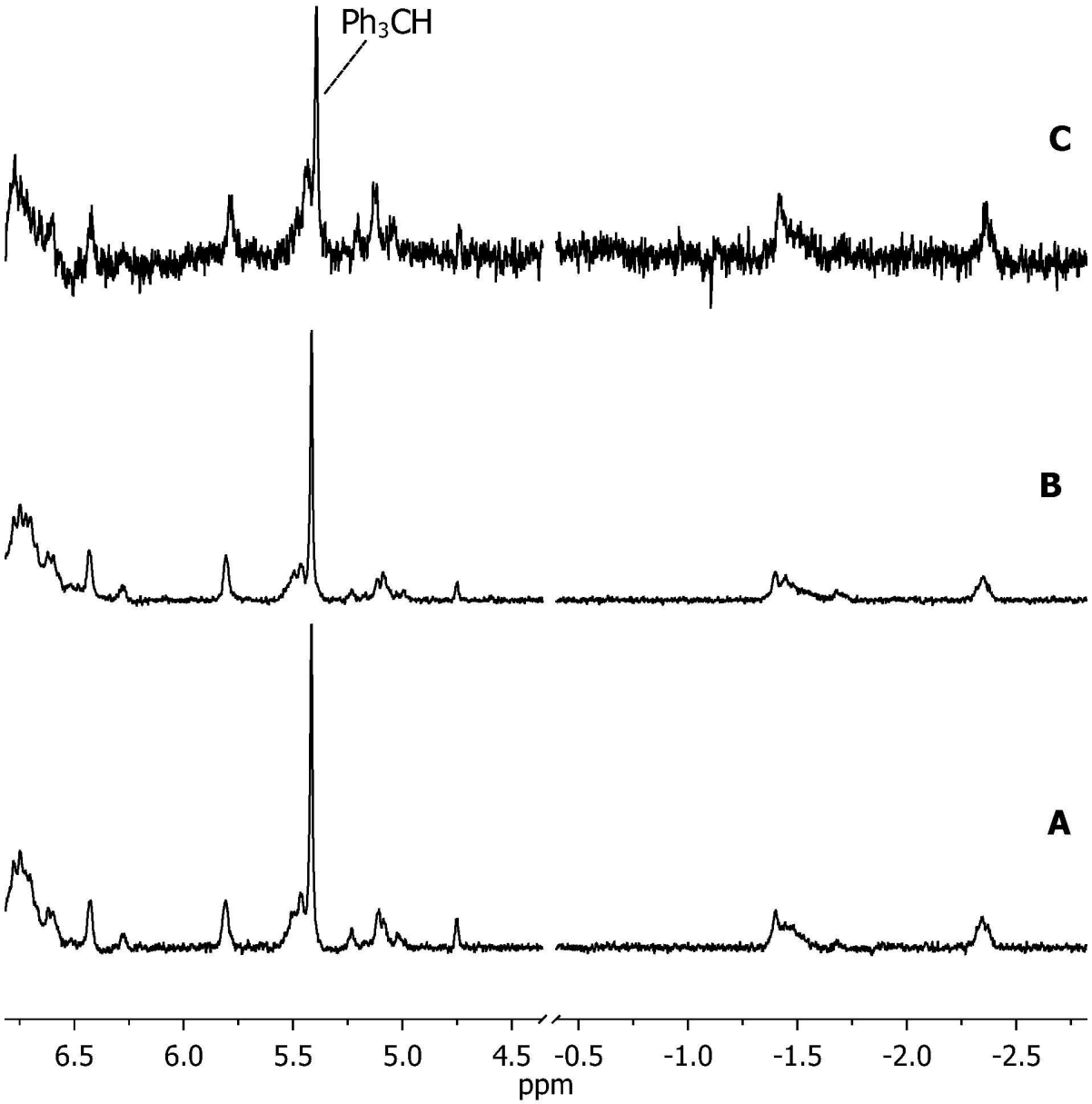

Figure S-28: ^{1}H NMR of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ + $AlOct_3$ with different equiv of HAl^iBu_2 to $AlOct_3$ of 5:10 (**A**), 10:10 (**B**) and 10:100 (**C**).

15. ^{1}H NMR spectrum of $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$ with R = n-octyl, isobutyl, methyl

A solution of $[(SBI)Zr(\mu\text{-}H)_3(AlR_2)_2]^+$ was prepared as above with 10 equiv $AlOct_3$ and 10 equiv HAl^iBu_2 (similar to Figure S-28A). To this solution was added 2.1 μL $AlMe_3$ (22 μmol, 10 equiv). A ^{1}H NMR spectrum was obtained (Figure S-29).

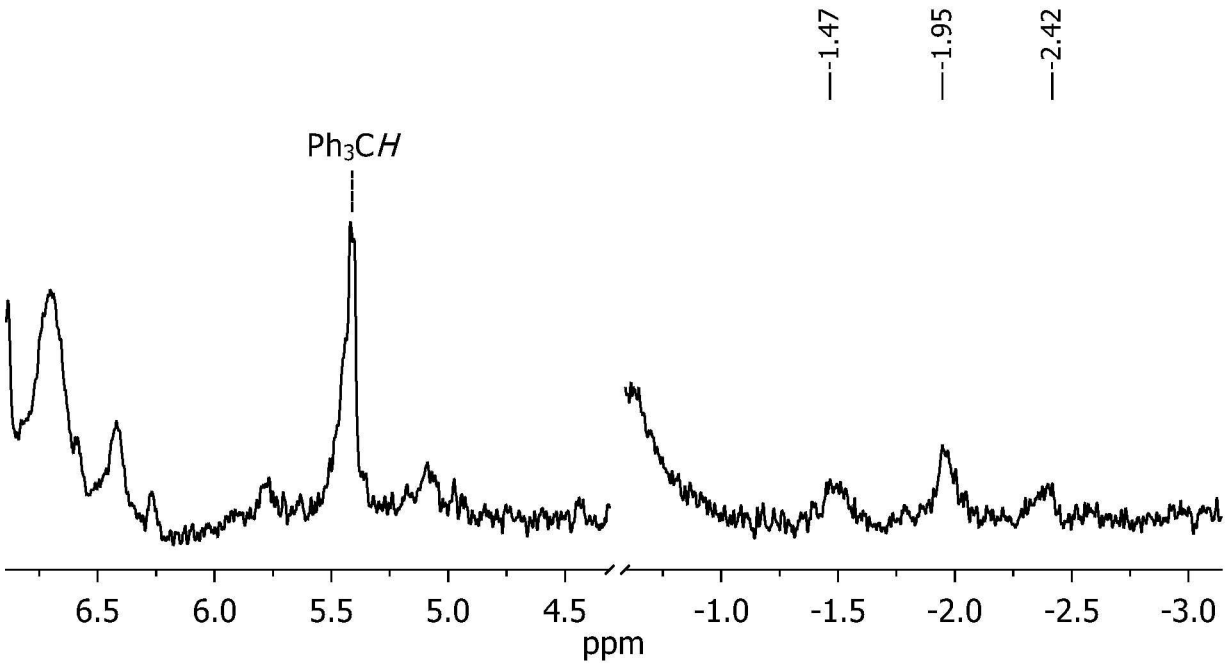

Figure S-29: ^{1}H NMR of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ + $AlOct_3$ + AlMe3 with 10 equiv of HAl^iBu_2, $AlOct_3$ and $AlMe_3$.

16. Determination of the Equilibrium Constant for the Reaction $[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2]^+ + (AlMe_3)_2 \leftrightarrows [(SBI)ZrMe_2AlMe_2]^+ + (HAlMe_2)_3$.

A solution containing 3.1 mM $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ was prepared by reacting 1.0 mg (2.2 μmol) of $(SBI)ZrCl_2$ and 3.0 μL (17 μmol, 5 equiv) of $(HAl^iBu_2)_2$ with 2.1 mg (2.2 μmol, 7.7 equiv) of $[Ph_3C][B(C_6F_5)_4]$ in 0.7 mL of toluene-d_8 in a J-Young NMR tube in the glove box. ^{1}H-NMR spectra were collected, at room temperature, after stepwise additions of 4.3 μL (45 μmol, 20 equiv) increments of neat $AlMe_3$ via microliter syringe in the glove box. Integrals of the Si-CH_3 signals for both zirconocene species, as well as of the *H*-Al and CH_3-Al signals at 3.72 and 0.31-0.34 ppm, respectively were monitored (Table S-1). All signals were invariant with reaction time and equilibrium was thus assumed to be established. The equilibrium constant K_{eq} was calculated, in accord with Scheme 8 of the main article, using the expression

$$K_{eq} = \frac{[(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+ \cdot [(HAlMe_2)_3]}{[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2]^+ \cdot [(AlMe_3)_2]}$$

For these calculations, values for 70–210 equiv of $AlMe_3$ were used, since the Si-C*H*$_3$ signal of $[(SBI)ZrMe_2AlMe_2]^+$ was first clearly observed at 70 equiv of $AlMe_3$ (Figure S-30), while at higher $AlMe_3$ concentrations $[(SBI)ZrMe_2AlMe_2]^+$ precipitated in the form of a red oil. The integrals of the C*H*$_3$-Al signals were corrected to represent the concentration of $(AlMe_3)_2$ by subtracting 2 times the integrals of the Si-C*H*$_3$ signal of $[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2]^+$ at 0.58 ppm and six times the integral of the *H*-Al signal of $(HAlMe_2)_3$ and division of the resulting value by 18. From eight such measurements, an average value of $K_{eq} = 0.97(15)*10^{-2}$ was determined.

Table S-1: Determination of K_{eq} from concentration data for a reaction system containing $[(SBI)Zr(\mu\text{-}H)_3(AlMe_2)_2]^+$ and 70 - 210 equiv of $AlMe_3$.

equiv $AlMe_3$	**Integrals**					**Normalized "Concentration" [a]**				**K_{eq}**
	Si(C*H*$_3$)$_2$			*H*-Al	C*H*$_3$-Al	$(SBI)ZrH_3^+$	$(SBI)ZrAlMe_4^+$	$(HAlMe_2)_3$	$(AlMe_3)_2$[b]	
	$ZrH_3Al_2Me_4$	$ZrAlMe_4$	Zr_{TOT}							
70	83.4	14.2	97.5	136.6	15315	13.9	2.4	45.5	796.0	0.0097
90	83.4	14.1	97.5	144.2	19166	13.9	2.4	48.0	1007.5	0.0081
110	80.3	17.2	97.6	148.8	23129	13.4	2.9	49.6	1226.4	0.0087
130	77.4	19.9	97.3	161.4	28183	12.9	3.3	53.8	1503.3	0.0092
150	74.8	22.6	97.3	167.0	32613	12.5	3.8	55.7	1747.8	0.0096
170	75.6	21.1	96.7	186.2	39694	12.6	3.5	62.1	2134.8	0.0081
190	67.3	30.5	97.8	162.4	37651	11.2	5.1	54.1	2030.1	0.0121
210	65.9	31.3	97.2	185.4	46103	11.0	5.2	61.8	2492.1	0.0118
									average **K_{eq}** ±	0.0097 ±0.0015

[a] "Concentration" refers to normalized integrals, such that tabulated concentrations are accurate relative to each other but are not absolute concentrations. Conversions to absolute concentrations were omitted, since any such factors would cancel out in determining the dimensionless value of K_{eq}. The total absolute concentration of Zr in all solution was 3.1 mM.

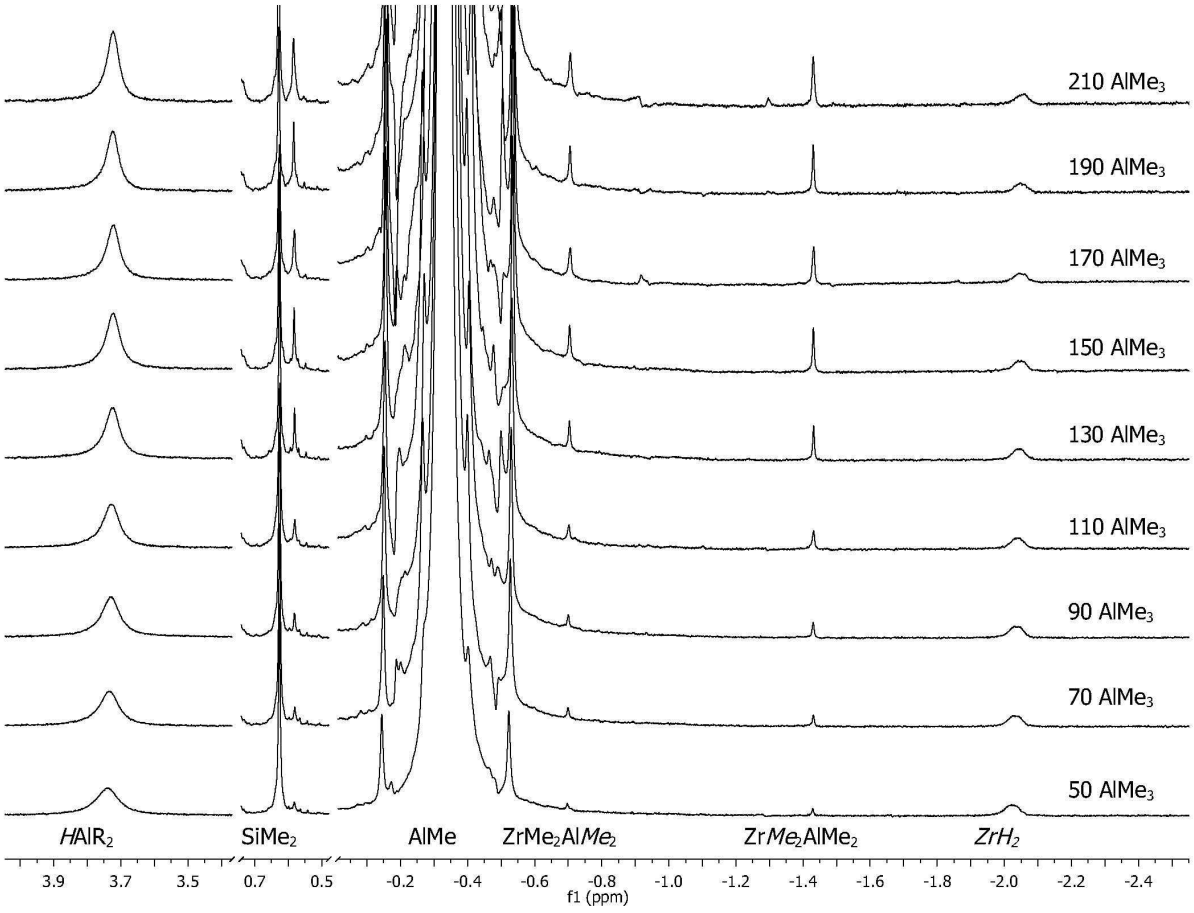

Figure S-30: ^{1}H-NMR spectra of a 3.1 mM solution of $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$ with 3.5 equiv of free HAl^iBu_2 upon addition of 50-210 equiv of $AlMe_3$ relative to Zr.

17. X-ray Crystallography Details

Data for [(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$][B(C$_6$F$_5$)$_4$]·½(C$_7$H$_8$) (**1**) and [(Me$_2$Si)$_2$(C$_5$H$_3$)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$] [B(C$_6$F$_5$)$_4$] (**2**) were collected on a Bruker KAPPA APEX II using Mo Kα X-ray source (λ = 0.71073 Å). The crystals were mounted on a glass fiber under Paratone-N oil and all data were collected at 100 K. Data were collected using ω scans. Data collection and cell parameter determination were conducted using the APEX2 program. Integration of the data frames and final cell parameter refinement were performed using SAINT software. Absorption correction of the data was carried out semi-empirically based on equiv reflections for **2** for **1** no absorption correction was applied. Subsequent calculations were carried out using SHELAXS software. Structure determination was done using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment with exceptions noted in the subsequent paragraph. A summary of relevant crystallographic data is presented in Table S-2.

For both complexes, the hydrides were located in the difference maps and their positions were refined. For **2** no restraints were applied while for **1** the thermal factors were restrained to be 1.2 times the U_{eq} of the corresponding metal atoms. Additionally in **1** all six-membered rings were constrained to be regular hexagons. The toluene was constrained to be flat and the atomic displacement parameters (ADP's) to simulate isotropic behavior. The eight isobutyl groups were restrained to have the same geometry with no target values for the bond lengths. The ADP's of the ^{i}Bu groups were restrained to simulate isotropic behavior however no restraints were placed on their sizes.

Table S-2: X-ray Crystallographic Data for all compounds

	[(SBI)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$	**[(Me$_2$Si)$_2$(C$_5$H$_3$)Zr(μ-H)$_3$(Al^{i}Bu$_2$)$_2$]$^+$**
Empirical Formula	$[C_{36}H_{57}Al_2SiZr][C_{24}BF_{20}]^-\cdot\frac{1}{2}(C_7H_8)$	$[C_{30}H_{54}Al_2Si_2ZrH_3]^+ [C_{24}BF_{20}]^-$
Crystal Habit, color	Block, yellow	Blade, colorless
Crystal Size (mm)	0.27 x 0.22 x 0.09	0.28 x 0.20 x 0.04
Crystal System	Orthorhombic	Monoclinic
Space Group	$P2_12_12_1$	$P2_1/n$
Volume (Å^3)	12669.3(9)	5766.9(5)
a (Å)	17.3916(7)	16.2579(8)
b (Å)	26.6355(12)	17.1922(7)
c (Å)	27.3497(12)	21.1975(10)
α (°)	90	90
β (°)	90	103.262(3)
γ (°)	90	90
Z	8	4
Formula weight (g/mol)	1388.20	1298.17
Density (calculated) (Mg/m^3)	1.456	1.495
Absorption coefficient (mm^{-1})	0.318	0.364
F_{000}	5656	2640
Total no. reflections	115139	75246
Unique reflections	23731	12697
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0623$, $wR_2 = 0.0749$ 13557 reflections	$R_1 = 0.0422$, $wR_2 = 0.0681$ 8862 reflections
R indices (all data)	$R_1 = 0.1201$, $wR_2 = 0.0779$	$R_1 = 0.0795$, $wR_2 = 0.0719$
Largest diff. peak and hole (e$^-$Å^{-3})	0.703 and -0.470	0.741 and -0.489
GOF	1.804	1.883

18. Selected distances and angles for the cation $[(SBI)Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$

Bond distances (Å)		nonbonding distances (Å)		bond angles (°)	
Zr1-H1H	1.92(4)	Zr1-Al1	3.1779(20)	H1H-Zr1-H3H	123.1(14)
Zr1-H2H	1.88(3)	Zr1-Al2	3.0945(19)	H1H-Zr1-H2H	56.7(13)
Zr1-H3H	1.99(4)			H2H-Zr1-H3H	66.4(14)
Al1-H1H	1.58(3)			H1H-Al2-H2H	60.4(16)
Al1-H2H	1.95(4)			H2H-Al1-H3H	70.7(15)
Al2-H2H	1.92(3)			ctr1-Zr1-ctr2	126.514(24)
Al2-H3H	1.73(3)				
Zr1-ctr1	2.1897(5)				
Zr1-ctr2	2.1913(5)		(ctr1: C1A-C5A, ctr2: C10A-C14A)		
Zr2-H4H	1.99(4)	Zr2-Al3	3.1015(20)	H4H-Zr2-H6H	129.4(14)
Zr2-H5H	1.92(3)	Zr2-Al4	3.1917(18)	H4H-Zr2-H5H	64.9(14)
Zr2-H6H	1.94(4)			H5H-Zr2-H6H	65.0(14)
Al3-H6H	1.75(3)			H5H-Al3-H6H	70.3(16)
Al3-H5H	1.85(4)			H4H-Al4-H5H	66.0(15)
Al4-H5H	2.07(4)			ctr3-Zr2-ctr4	126.868(24)
Al4-H4H	1.78(3)				
Zr2-ctr3	2.1883(5)				
Zr2-ctr4	2.2055(5)		(ctr3: C1B-C5B, ctr4: C10B-C14B)		

19. Selected distances and angles for the cation $[(Me_2Si)_2(C_5H_3)_2Zr(\mu\text{-}H)_3(Al^iBu_2)_2]^+$

Bond distances (Å)		nonbonding distances (Å)		bond angles (°)	
Zr1-H1H	1.9786(1)	Al1-Zr1	3.0893(1)	H1H-Zr1-H2H	64.795(2)
Zr1-H2H	2.0850(1)	Al2-Zr1	3.0831(1)	H1H-Zr1-H3H	128.616(3)
Zr1-H3H	1.9495(1)			H2H-Zr1-H3H	63.840(2)
Al1-H1H	1.6449(1)			H1H-Al1-H2H	75.844(2)
Al1-H2H	1.8871(1)			H1H-Al2-H3H	74.995(2)
Al2-H2H	1.8290(1)			ctr1-Zr1-ctr2	122.646(2)
Al2-H3H	1.6747(1)				
Zr1-ctr1	2.1568(1)				
Zr1-ctr2	2.1543(1)		(ct1: C1-C5, ctr2: C6-C10)		

1) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc*. **1971**, *93*, 2046.
2) (a) Wartik, T.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1953**, *75*, 835. (b) Grady, A. S.; Puntambekar, S. G.; Russell, D. K. *Spectrochimica Acta* **1991**, *47A*, 47. (c) Downs, A. J.; Greene, T. M.; Collin, S. E.; Whitehurst, L. A.; Brain, P. T.; Morrison, C. A.; Pulham, C. R.; Smart, B. A.; Rankin, D. W. H.; Keys, A.; Barron, A. R. *Organometallics* **2000**, *19*, 527. (d) Vass, G.; Tarczay, G.; Magyarfalvi, G.; Bödi, A.; Szepes, L. *Organometallics* **2002**, *21*, 2751.